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(71) Applicant: L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE [FR/FR]; 75, quai d'Orsay, F-75321 Paris Cédex 07 (FR).

(72) Inventor: SPENCER, Kevin, C. ; 138 The Lane, Hinsdale, IL 60521 (US).

(74) Agent: LE MOENNER, Gabriel; L'Air Liquide, Société Anonyme pour l'Etude et l'Exploitation des Procédés Georges Claude, 75, quai d'Orsay, F-75321 Paris Cédex 07 (FR).

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(54) Title: METHOD OF IMPROVING THE AROMA AND FLAVOR OF STORED BEVERAGES AND EDIBLE OILS

(57) Abstract

A method of improving the aroma and flavor of beverages or edible oils or both, which entails contacting the same during at least a portion of processing or storage thereof with a noble gas, a mixture of noble gases or a mixture containing at least one noble gas.

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TITLE OF THE INVENTION

METHOD OF IMPROVING THE AROMA AND FLAVOR OF STORED BEVERAGES AND EDIBLE OILS

BACKGROUND OF THE INVENTION

The ability of the noble gases helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Ra) to enter into chemical combination with other atoms is extremely limited. Generally, only krypton, xenon and radon have been induced to react with other atoms, which are highly reactive, such as fluorine and oxygen, and the compounds thus formed are explosively unstable. See Advanced Inorganic Chemistry, by F.A. Cotton and G. Wilkinson (Wiley, Third Edition). While, xenon is known to exhibit certain physiological effects, such as anesthesia, the noble gases are generally considered to be inert.

Beverages and edible oils are conventionally preserved during storage by using inert or non-reactive gases to merely displace atmospheric oxygen from their immediate vicinity. It is known that oxygen can degrade many of the aroma and flavor components of the substances.

For example, JP 3058778 (89192663) describes the storage and maturation of alcoholic drinks, such as sake, in an argon atmosphere, whereby the argon is used simply to displace oxygen.

JP 58101667 (88019147) describes sealing of citrus drinks under pressure of argon or nitrogen as an inerting agent so that bubbles are released upon depressurization which cling attractively to the pulp.

JP 60134823 describes packaging of liquid food wherein argon or nitrogen as inert gases are used to push the product into the package.

JP 7319947 (730618) describes fruit juice preservation under inert gases, wherein Argon, Helium and Nitrogen are considered equally inert.

US 3128188 describes lagering of Ruh beer under an inert atmosphere.

US 309181 describes a process for gas-packaging tomato juice or liquid food products or vegetable concentrates, wherein any inert gas or non-reactive gas including Argon, Nitrogen, Krypton, or Helium or mixtures thereof are completely equivalent.

US 3535124 describes a fresh fruit juice dispensing system in which inert gas is used to deoxygenate during spraying.

US 4803090 discloses that during cooking of foods in oils, any inert gas may be used with equivalence to displace oxygen. No significant change in the oil was noted.

Cooling of liquid foods may also be achieved using any inert or non-reactive gas. For example, see DE 2147880, ZA 7106193, FR 2107946 and GB 1371027.

US 4901887 describes a beverage dispenser which is pressurized with any inert or non-reactive gas.

WO 8600503, DE 3425088, AU 8546026, EP 189442 and DE 3448380 each disclose the use of inert or non-reactive gases in the heating of liquid food products while maintaining aroma and preventing boiling. Nitrogen or noble gases may be used equivalently as inert non-reactive gases.

DE 2736282, WO 7900092, HU H2477, GB 2021070, DD 137571, DD 137571 and EP 6888 each describe a beer road tanker charging system which uses an inert or non-reactive gas constituting any of carbon dioxide, nitrogen or noble gas, as equivalent as inert or non-reactive gases.

GB 1331533, FR 2089899, BE 765637, DE 2031068 and CH 522734 each describe a method of preserving alcoholic beverages wherein oxygen is displaced at any process stage, including storage, by preferably nitrogen. Argon or another noble gas may be used, as all are deemed to be equivalently inert or non-reactive.

Thus, at present, removal of oxygen from the atmosphere in contact with beverages and edible oils is recognized as desirable. This may be done, as noted above, by physically displacing oxygen with an inert or non-reactive gas. Generally, nitrogen is used preferentially because of its low cost and availability, except when carbon dioxide may be used, as it is even less expensive. For example, carbon dioxide may be used in sparkling beverages. While argon and noble gases have been used, they are explicitly described in the art as being as inert or non-reactive gases like nitrogen, or as carbon dioxide, and are used as such.

Orange juice is extracted by various mechanical means from whole oranges in a process which is usually exposed to

oxygen. Bartholomai, A. 1987. Food Factories-Processes, Equipment, Costs (VCH Publishers, New York, N.Y.). The aroma losses due to oxidation are of greatest concern during processing and particularly during storage.

Orange juice is a complex mixture and over 150 constituents of orange juice volatiles have been reported and identified, among which 40 terpene hydrocarbons, 30 esters, 36 aldehydes and ketones, 36 alcohols and 10 volatile organic acids have been isolated. An example of a chromatogram of the extracted volatiles form orange juice is given by Papanicolaou et al., J. Food Technol. 13:51IL 519 (1978).

During storage of orange juice, aroma and flavor compounds undergo many oxidative chemical reactions, which lead to the deterioration of the aroma. These reactions may be caused by either atmospheric oxygen or by oxygen from chemical sources.

Before pasteurization of orange juice, products of oxidative enzymatic reactions can accumulate and form off-flavor compounds during storage. Bruemmer et al, J. Food Sci. 41:186-189 (1976). In unpasteurized orange juice, accumulation of acetaldehyde is probably responsible for the production of diacetyl in orange juice during storage. Diacetyl can result from oxidation of acetoin.

Orange juice contains ascorbic acid (vitamin C) which is an important antioxidant. Often, large amounts of this compound are added to commercial juice. However, it would be preferable to avoid such large additions, or to limit them, and to directly control of the chain of oxidative

reactions involving ascorbic acid. Of course, oxygen degradation of aroma components in the headspace is not retarded at all by ascorbic acid, which is in solution.

Citrus juices are particularly susceptible to degradative oxidation caused by the action of oxidase enzymes or by oxygen present in the atmosphere or in solution. Displacement of this oxygen results in only a partial retardation of oxidation.

The principal problems of production quality in the citrus processing industry are clarification, color, taste, bitterness, loss of flavor, oxidation of flavor.

Proper cloud retention is a crucial quality parameter of citrus juice, which processors address by control of clarification. Loss of the appealing cloudiness of orange or other citrus juice occurs during storage due to the enzymatic action of pectinesterase. The product of pectinesterase activity is pectic acid, which chelates with divalent cations to form insoluble pectates, responsible for undesirable fruit clarification.

Presently, the only means available to stabilize (inactivate) the enzyme is heat. Unfortunately, heat is also responsible for the loss of intrinsic citrus aromas, which render citrus juices so appealing.

Naringin is the main factor responsible for bitterness in several citrus juices. Naringinase is commonly used in the citrus industry to reduce bitterness. When present in large amounts, naturally occurring naringin, or 4',5,7-trihydroxyflavanone-7-rhamnoglucoside, is responsible for a bitter taste, which is an unappealing customer trait of

grapefruit and other juices. Naringinase is an enzyme complex that contains two types of enzymatic activities (α-rhamnosidase and ß-glucosidase activities), and those catalyze the breakdown of naringin into glucose and naringenin, which are not bitter.

Citrus juices can also be debittered by being passed through a hollow fiber system containing immobilized naringinase.

In preserving orange or other citrus juice, several factors are important, i.e., consistency of sweetness, tartness, color, and characteristic flavor to the consumer. Orange or other citrus juice is expected to be cloudy with suspended solids. The carbohydrate gum, pectin, helps maintain the suspension. An enzyme, pectinesterase, attacks pectin causing the juice to clarify. Some other juices are preferred to be clear (apple and cranberry, for instance). In these, enzymes may be added to promote clarification.

During storage of orange or other citrus juice, aroma and flavor compounds undergo many oxidative chemical reactions, which lead to the deterioration of the aroma. These reactions may be caused by either atmospheric oxygen or by oxygen from chemical sources.

Before pasteurization of orange or other citrus juice, products of oxidative enzymatic reactions can accumulate and form off-flavor compounds during storage (Bruemmer et al., 1976). In unpasteurized orange or other citrus juice, accumulation of acetaldehyde appears to be responsible for the production of diacetyl in orange or other citrus juice

during storage. Diacetyl can result from oxidation of acetoin (Papanicolaou et al., 1978).

Moreover, orange, as well as other citrus juice, contains ascorbic acid (vitamin C) which is an important antioxidant. Often, large amounts of this compound are added to commercial juice. It would be desirable to avoid or reduce the amount of ascorbic acid added in order to have greater control over oxidative reactions involving ascorbic acid. It is also noted that oxygen degradation of aroma components in the headspace is not retarded by ascorbic acid, which is in solution.

At the same time, oxidation of oils is the major spoilage phenomenon of concern in the industrial manufacture or storage of oils. The presence of oxygen causes oxidative conversion of lipids and oils, for instance triglycerides, into oxides, acids, and other degraded forms. Enzymatic oxidations are particularly rapid and damaging, involving such enzymes as lipoxygenases, peroxidase, and other oxidases.

Generally, oxygen is excluded by eliminating headspace, vacuum storage, or storage under nitrogen. Elimination of headspace requires careful monitoring of processes and may create overpressure problems or leakage during container filling. Vacuum storage is expensive and many oils are volatile or contain volatile aroma components. Storage under nitrogen is the best solution available today, however, it is not completely satisfactory, and is not effective in altering enzymatic degradation rates.

Presently, oils are extracted through pressing, centrifugation, filtration, solvent extraction or flocculation or a combination thereof. The presence of oxygen causes oxidative conversion of lipids and oils, for instance triglycerides, into oxides, acids, and other degraded forms. Oxidative degradation is the most important degradative phenomenon. This occurs even when atmospheric oxygen is excluded as the oxygen sources are present within the oil. Enzymatic oxidations are particularly rapid and damaging, involving such enzymes as lipoxygenases, peroxidase, and other oxidases. This is, or course, a particularly troublesome problem with seed oils and vegetable oils intended for human consumption.

Generally, oxygen is excluded from contact with oils by eliminating headspace, vacuum storage, or storage under nitrogen. Elimination of headspace requires careful monitoring of processes and may create overpressure problems or leakage during container filling. Vacuum storage is expensive and many oils are volatile or contain volatile aroma components. Storage under nitrogen is the best solution available today, however, it is not completely satisfactory, and is not effective in altering enzymatic degradation rates.

U.S. 4803090 discloses that during cooking of foods in oils, any inert gas may be used with equivalence to displace O_2. Specifically, no significant change in the oil was noted.

EP 189442 describes the use of inert gases in the heating of liquid food products while maintaining aroma and

preventing boiling, wherein N_2 or noble gases may be used equivalently.

Several citations are known which utilize argon as an inerting control in studies of oxygen-induced oxidation. In these studies, however, no effect of argon other than simple inerting is demonstrated or claimed. For example, Peers and Swoboda (1982); Unbehend et al. (1973); Schsnept et al. (1991).

Unfortunately, however, while it is considered desirable to remove oxygen from the headspace atmosphere of stored edible oils, particularly seed oils, by displacing the same with an inert gas, such as nitrogen or carbon dioxide or a gas deemed to also be inert, simple displacement of atmospheric oxygen does not provide an adequate means of protection against seed oil oxidation.

In fact, seed oils and vegetable oils oxidize readily under normal manufacturing process conditions. This oxidation lowers the actual and commercial quality of finished product. Oxidation proceeds most readily in the presence of air or other source of oxygen, and modern processes are conducted so as to minimize this contact. In the past, blanketing with inert gas has been used in final storage steps in order to minimize oxygen contact. However, these uses of inert gas are not particularly effective, nor are they economical. Instead, simple air exclusion by equipment design is the preferred method of minimizing contact of the oil with oxygen. This is sometimes combined with the nitrogen blanketing to prevent the access of oxygen to the oil. Other methods have been employed, including

steam stripping of air, but thermal degradation also enhances oxidation, thus this method is also not entirely effective.

It is also well-known that oxidation of oil proceeds even in the absence of air, since molecular oxygen is found in water or oil products themselves, or may be donated from other molecules which are oxygen donors under process conditions. Current methods cannot control these oxidative processes adequately.

While different from wine, beer is also a highly volatile fermented product in terms of flavor constituents, and is prepared according to well-understood brewing processes (Bartholomai, 1987). Continuous or batch fermentation using Saccharomyces yeast is regulated and optimized across all possible parameters including the possible storage at any stage of the working solutions or mashes. Storage under nitrogen is possible to prevent oxidation and is practiced occasionally, but most manufacturers rely upon heat or off-gases to exclude oxygen, and accept a relatively high level of oxidation as inevitable.

Hence, a need exists for a means by which diverse beverages and edible oils may be preserved and/or maintained, to improve the aroma and flow thereof. In particular, a need exists for a means by which greater control can be obtained over the various oxidative reactions involved in the degradation of citrus juices, generally, and, specifically, over oxidative reactions involving ascorbic acid. A need also exists for a means by which

diverse juices may be preserved and/or maintained to thereby improve the aroma and flavor thereof.

Moreover, a need exists, in particular, for a means by which edible oils, particularly seed oils, may be preserved in order to improve the aroma and flavor thereof.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method for preserving beverages and edible oils.

It is also an object of the present invention to provide a method for imporving the aroma and flavor of stored beverages and edible oils.

Moreover, it is a particular object of the present invention to provide a method for improving the aroma and flavor of citrus juice, beer and edible oils.

The above objects and others are provided by a method for preserving beverages and edible oils, which entails contacting the beverages or edible oils during at least a portion of processing or storage thereof with a noble gas, mixture of noble gases or mixtures containing at least one noble gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a UV/VIS spectra of beer oxidation after 30 days storage under different gases as indicated.

Figure 2 illustrates a GC/MS chromatogram plot of beer volatiles after 30 days storage under argon.

Figure 3 illustrates a GC/MS chromatogram plot of beer volatiles after 30 days storage under nitrogen.

Figure 4 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 5 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 6 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 7 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 8 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 9 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 10 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 11 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under oxygen.

Figure 12 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under oxygen.

Figure 13 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 14 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 15 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 16 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 17 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 18 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 19 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 20 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 21 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 22 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 23 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 24 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 25 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 26 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 27 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 28 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 29 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 30 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 31 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 32 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 33 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 34 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 35 is a schematic illustration of a process for manufacturing soybean oil from soybeans.

Figure 36 is a schematic illustration of a process for manufacturing refined salad oil or refined margarine or shrotening oil from crude soybean oil.

Figure 37 is a schematic illustration of a production process of orange juice from oranges.

Figure 38 illustrates a GC/MS of oragne juice aroma volatiles under argon.

Figure 39 illustrates a GC/MS of orange juice aroma volatiles under nitrogen.

Figure 40 illustrates a GC/MS of orange juice aroma volatiles under oxygen.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Beverages and edible oils are particularly subject to degradative oxidation by either enzymatic degradation by oxidases, or to chemical oxidation by oxygen from headspace, solution, or autogenous sources while physical displacement of oxygen partly retards oxidation, the effect provided is generally inadequate.

In accordance with the present invention, however, a method has been surprisingly discovered for preserving

beverages and edible oils, which entails contacting the beverages or edible oils during at least a portion of storage thereof with a noble gas, mixture of noble gases or mixtures containing at least one noble gas.

Generally, as used herein, the phrase "contacting the beverages or edible oils" is intended to include contacting the headspace, or the liquid surface or even below the surface of the beverages or edible oils. Notably, any one or any combination of these definitions is explicitly intended to fall within the definition and scope of this phrase.

Also, as used herein, the term "noble gas" is intended to include argon, xenon, krypton and neon. Helium may be used although it is not preferred due to its ease of escape. Radon is not used as it is dangerously radioactive.

In accordance with the present invention, argon, xenon, krypton and neon may be used alone or in any combination. For example, binary mixtures of argon-xenon, krypton-xenon or xenon-neon may be used, or ternary mixtures of argon-xenon-krypton may be used, for example.

However, mixtures containing at least one noble gas with one or more other carrier gases may also be used. Carrier gases may include, for example, nitrogen, oxygen, carbon dioxide, nitrous oxide and even helium.

Generally, the effect of the present invention may be obtained at a range of pressures form about near-vacuum, i.e. about 10^{-8} tow, to about 100 atmospheres. However, it is generally preferred that a pressure be used between about 0.001 to about 3 atmospheres. Further, a range of

temperature is generally used which is the same as the operable and preferred temperatures of storage for beverages and edible oils and for different stages of processing. For example, such temperatures may range from freezing temperatures to cooking temperatures. However, lower temperatures and ambient temperatures are generally used for storage.

As noted above, a single noble gas, such as argon, or a mixture of noble gases may be used in accordance with the present invention. However, mixtures containing at least one noble gas and one or more carrier gases may also be used.

Any relative mix of the gases may be used as long as the preserving effect of the noble gas component or components outweighs any oxidative effects of the carrier gases, such as oxygen. Generally, however, each noble gas may be used in such mixtures in the amount of from above 0 to 100 volume % or at any value in between. Further, any relative mix, i.e. of from above 0 % to 100 volume %, may be used for the binary mixtures. Of course, the total amount of the gas is 100 volume %.

For example, in accordance with the present invention it is advantageous to use inexpensive production plant offstream gases having a composition of about 90% kr and 10% Xe in volume %, based on the total gas volume.

It is also advantageous to use mixture containing an effective amount of one or more nobel gases in deoxygenated air. Generally, as used herein, the term "deoxygenated air" is intended to mean air having generally less than 15 volume

% or 10 volume %, preferably less than 5 volume % oxygen therein.

Further, the gas or gas mixtures of the present invention may be used as gases or may also be introduced in the beverage or edible oil or into the headspace or even above in storage means in order to form the described atmosphere.

Color improvement in beer, olive oil and other oils, and especially orange juice, is dramatic and represents by itself a very surprising and significant improvement.

Flavor is also improved according to a blind taste test of each product.

As in the application jointly deposited, storage of any liquid foodstuff or beverage under any of the noble gases argon, xenon, krypton, neon, or helium, alone or in mixtures, or admixed with nitrogen or small amounts of oxygen or carbon dioxide or nitrous oxide greatly improve the retardation of oxidation as compared to that obtainable using nitrogen.

Notably, the effect of the present invention is demonstrated over a wide range of temperatures, including during cooking or pasteurization, refrigeration, and freezing, including cryogenic freezing. It is also observed under low or very high pressures.

The present invention may be used to enhance the aroma and flavor of any type of beverage and/or edible oil, particularly during storage. In particular, however, the present invention is especially advantageous in improving

the aroma and flavor of citrus fruit juices and edible oils, such as seed oils.

I. USE OF THE PRESENT INVENTION IN PRESERVING THE AROMA AND FLAVOR OF CITRUS JUICE

In accordance with one aspect of the present invention, a method is provided for preserving citrus juice or a precursor thereof by controlling the oxidative reactions which generally contribute to the degradation of citrus juices, particularly those involving ascorbic acid. Quite surprisingly, it has been discovered that this can be accomplished by contacting the citrus juice or precursor material thereof with a noble gas, mixture of noble gases or gas containing at least one noble gas during at least a portion of a production process for the citrus juice or storage of the juice or precursor.

As used herein, the term "noble gas" is intended to include argon, xenon, krypton and neon. Helium does not work, and radon is radioactive and not useful.

It is explicitly contemplated herein that the term "citrus" be interpreted as broadly as is scientifically recognized. Thus, lemons, oranges, limes, grapefruit, tangerines, and tangelos, for example, may be used. Also, the term "citrus" is intended to include parts of fruit, such as rinds and pulp, as well as extracts therefrom.

In accordance with the present invention, argon, xenon, krypton and neon may be used alone or in any combination. For example, binary mixtures of argon-xenon, krypton-xenon

or xenon-neon may be used, or ternary mixtures of argon-xenon-krypton may be used, for example.

However, mixtures containing at least one noble gas with one or more other carrier gases may also be used. Carrier gases may include, for example, nitrogen, carbon dioxide, nitrous oxide, helium and oxygen at low concentration. Preferably, however, the carrier gas is an inert gas, such as nitrogen.

Generally, the effect of the present invention may be obtained at a range of pressures form about near-vacuum, i.e., about 10^{-8} torr, to about 100 atmospheres. However, it is generally preferred that a pressure be used between about 0.001 to about 10 atmospheres, more preferably between about 0.001 to about 3 atmospheres. Further, a range of temperature is generally used which is from freezing temperatures to cooking temperatures, such as about -20°C to about 300°C. However, lower temperatures and ambient temperatures are generally used for storage.

As noted above, a single noble gas, such as argon, or a mixture of noble gases may be used in accordance with the present invention. However, mixtures containing at least one noble gas and one or more carrier gases may also be used.

In accordance with the present invention, it has also been unexpectedly discovered that if instead of solely blanketing the headspace above a citrus juice or precursor stored in containing means, such as a tank or a bottle with any kind of inert gas, a gas or gas mixture containing an element selected from the group consisting of argon,

krypton, xenon and neon or a mixture thereof is sparged into the citrus juice or precursor and/or injected above the citrus juice and/or precursor in order to saturate or substantially saturate said citrus juice and/or precursor with the gas or gas mixture, it is possible to substantially improve the color and/or the flavor and/or the aroma and/or the shelf life of the citrus juice and/or precursor, particularly when the saturation or substantial saturation is maintained throughout the volume of the storage container and during substantially all the time that the citrus juice and/or precursor is stored in said container.

The term "substantially saturate" means that it is not necessary to completely and/or constantly saturate the citrus juice and/or precursor with the gas or gas mixture (i.e., having the maximum amount of gas solubilized in the citrus juice and/or precursor). Usually, it is considered necessary to saturate the citrus juice and/or precursor to more than 50% of its (full) saturation level and preferably more than 70%, while 80% or more is considered the most adequate level of saturation of the citrus juice or precursor. Of course, supersaturation is also possible. This means that if during the storage life of the citrus juice or precursor in the container, the citrus juice or precursor is not saturated with noble gas at least from time to time or even quite longer if it remains generally substantially saturated, results according to the invention are usually obtained. While it is believed that it is important that the entire volume of the container be saturated or substantially saturated with one of the above

gas or a mixture thereof, it is quite possible to obtain the results according to the invention if a part of the volume is not saturated during preferably a limited period of time or is less saturated or substantially saturated than other portions of the volume of the citrus juice or precursor in the container.

While at least one of the above gases must be present in order to obtain the benefits of the invention, said gases can be diluted with some other gases, in order to keep for example the invention economically valuable. Said diluent gases are preferably selected from the group comprising nitrogen, oxygen, nitrous oxide, air, helium or carbon dioxide. In case of an oxygen-containing gas or another reactive gas such as carbon dioxide, their degradative properties are such that these properties will mask the effect of noble gases, certainly in mixtures where they comprise 50% vol. or more and possibly 30% vol. or more. When those mixes comprise 0% to 10% vol. of these other gases, the noble gases referred to above are still extremely effective, while between 10% vol. and 20% vol. they are usually still effective, depending on the type of gases and conditions, which might be easily determined by the artisan.

In case of nitrogen and/or helium gas, the effect of noble gases consisting of Ar, Ne, Kr, Xe in the mixture is linearly proportional to its concentration in the mixture, which evidences that nitrogen and/or helium have no effect on substantially preventing oxidation of citrus juice and/or precursor thereof. The mixture of noble gas and nitrogen and/or helium can thus comprise any amount (% volume) of

nitrogen and/or helium: however, in practice, the lesser the proportion of noble gas selected from the group consisting of Ar, Ne, Kr and Xe, the larger the time required to achieve saturation or substantial saturation of the citrus juice and/or precursor thereof.

Among the active gases (Ar, Kr, Xe, and Ne), it is preferred to use argon because it is cheaper than the other active gases. However, mixtures of argon and/or krypton and/or xenon are at least as effective as argon alone. It has also been unexpectedly found that mixtures comprising between 90 to 99% vol. argon and 1 to 10% Xe and/or Kr are usually the most effective as exemplified in the further examples (whether or not they are diluted with nitrogen, helium, or nitrous oxide). The difference in effect between the active gases defined hereabove and nitrogen have been also evidenced by the fact that mixtures of argon and oxygen or carbon dioxide have a similar (while decreased) effect than argon alone, while nitrogen mixed with oxygen or carbon dioxide evidenced no protective or preservative effect compared to oxygen or carbon dioxide alone.

It is believed that the saturation or substantial saturation of the citrus juice and/or precursor is an essential feature of the invention and that no one in the prior art has ever disclosed nor suggested said feature.

Generally speaking, Xe is the most efficient gas according to the invention, followed by Kr, Ar and Ne. Among the suitable mixes, either pure or diluted with N_2, He, N_2O (or even air, oxygen or a small amount of hydrogen) are the Ne/He mix comprising about 50% vol. of each, and the

Kr/Xe mix comprising about 5-10% vol. Xe and about 90-95% vol. Kr, with a small amount of argon and/or oxygen (less than 2% vol.) or nitrogen (less than 1% vol.).

The temperatures at which the invention is carried out is usually between about 0°C to 60°C, and preferably about 10°C and 30°C.

The injection of the gas or gas mixture into the wine and/or into the container, e.g. by sparging is usually done at about 1 atmosphere but is still quite operable at 2 or 3 atmospheres, while saturation is increased at higher pressures. The pressure of the gas above the citrus juice and/or precursor in the container shall be, in any case, preferably lower than 10 atmospheres and it is usually acceptable to maintain it lower than 3 atmospheres.

Saturation or substantial saturation of the wine can be measured by various methods well-known by the man skilled in the art, including but not limited to thermogravimetric analysis or mass change weighting.

There are a variety of standard methods available for the detection, qualitative and quantitative measurement of gases, and several are especially well suited for the determination of degree of saturation of noble gases into liquid samples.

Samples generally are completely evacuated as a control for zero % saturation. Such samples may then be completely saturated by contact with noble gases such that no additional noble gas will disappear from a reservoir in contact with the sample. Such saturated samples may then have their gas content driven off by trapped evacuation or

by increase in temperature, and said gas sample identified quantitatively and qualitatively. Analysis is of trapped gases, reservoir gases, or some other headspace of gases, not directly of the sample.

Direct sample analysis methods are available, and include comprehensive GC/MS analysis, or by mass or thermal conductance or GC analysis and comparison with calibrated standards.

The simplest method is GC/MS (gas chromatography/mass spectrometry), which directly determines gas compositions. By preparing a standard absorption curve into a given sample for a series of gases and mixtures, one can accurately determine the degree of saturation at any point in time.

GC/MS is applied to the gas itself, as in the headspace above a sample. The technique may be used either to determine the composition and quantity of gas or mixture being released from a sample, or conversely the composition and quantity of a gas or mixture being absorbed by a sample by following the disappearance of the gas.

Appropriate GC/MS methods include, for example, the use of a 5 Angstrom porous layer open tubular molecular sieve capillary glass column of 0.32 mm diameter and 25 meter length to achieve separation, isothermally e.g. at 75°C or with any of several temperature ramping programs optimized for a given gas or mixture e.g. from 35-250°C, wherein ultra-high purity helium or hydrogen carrier gas is used at e.g. 1.0 cc/min flow rate, and gases are detected based upon their ionicity and quantitative presence in the sample, and characterized by their unique mass spectra.

Appropriate experimental conditions might include, for example, completely evacuating a given sample under vacuum to remove all absorbed and dissolved gases, then adding a gas or mixture to the sample and measuring a) the rate of uptake of each component as disappearance from the added gas, and/or b) the final composition of the gas headspace after equilibration. Both measurements are made by GC/MS, and either method can be used in both batch and continuous modes of operation.

A simplification of this analysis entails the use of a GC only, with a thermal conductivity detector, wherein adequate knowledge of the gas saturation process and preparation of calibration curves have been made such that quantification and characterization of gases and mixtures can be accomplished without mass spectral analysis. Such instruments are relatively inexpensive and portable.

A further simplification would depend solely upon measurement of the mass change in the sample upon uptake of various gases or mixtures, which depends upon the use of standard curves or absorption data available from the literature.

An alternate method for such mass measurements is thermogravimetric analysis, which is highly precise, wherein a sample is saturated with gas and mass changes are correlated to thermal change.

For example, in accordance with the present invention it is advantageous to use inexpensive production plant off stream gases having a composition of about 90% Kr and 10% Xe in volume %, based on the total gas volume or Ne:He 1:1.

It is also advantageous to use mixture containing an effective amount of one or more noble gases in deoxygenated air. Generally, as used herein, the term "deoxygenated air" is intended to mean air having generally less than 15 volume % or 10 volume %, preferably less than 5 volume % oxygen therein.

Further, the gas or gas mixtures of the present invention may be used as gases or may also be introduced into the citrus juice or precursor thereof or into the headspace or even above in storage means in order to form the described atmosphere.

Color improvement in the citrus juices is quite dramatic, which is, itself, a very surprising and significant improvement. Further, flavor is also improved according to a blind taste test of each product.

Storage of any citrus juice under any of the noble gases argon, xenon, krypton, neon, alone or in mixtures, or admixed with nitrogen or small amounts of oxygen or carbon dioxide or nitrous oxide greatly, and surprisingly, improve the retardation of oxidation as compared to that obtainable using nitrogen.

As already noted, the effect of the present invention is demonstrated over a wide range of temperatures, including during cooking or pasteurization, refrigeration, and freezing, including cryogenic freezing. It is also observed under low or very high pressures.

Generally, the advantages of the present invention may be obtained by contacting whole citrus fruit, portions of citrus fruit, concentrate and/or juice with the gases of the

present invention at any, and preferably every, stage of the production process beginning with the peeling of the fruit.

As used herein, the term "precursor" means any natural product which may serve as a source of citrus juice or as a flavoring additive for citrus juice. Examples of precursors are whole citrus fruit, portions of the fruit including flesh, seeds or rinds or even citrus oils or citrus blossoms or even extracts therefrom.

In order to further describe the present invention, the following typical production process for frozen concentrated orange juice will now be described solely to illustrate the present invention without limiting the same.

This process is illustrated by reference to Figure 1.

Step 1: Unloading system for trucks.

Step 2: Storage facilities (e.g., water basin storage system) and cleaning, grading, and sizing of oranges.

Step 3: Orange peel is rich in a very automatic oil, which if present in large quantities, gives a bitter taste to the juice. Nevertheless a small amount of oil is necessary to give orange juice its original taste. Furthermore, orange essential oil is a product with a non-negligible added value, since it is used in other products as an aroma chemical. Therefore, the juice extraction machinery is designed to insure an adequate separation of the juice from the peel oil.

This first step in the extraction process is to remove the peel external layer by passing the oranges through a scarifier. The oil is transported as an emulsion (formed by

spraying water) to the essential oils recovery line, where it is centrifuged.

Scarified oranges go through the juice extractor.

Step 4: Seeds and large particles such as the membrane and the core of the fruit are separated from the juice and small pulp particles through the finishing step.

Step 5: The juice in then pumped to holding tanks, where it can be blended in order to achieve uniformity (standardized color and total solids; standardized sugar and acid contents).

Step 6: The pasteurization step, which is used when marketing "pasteurized" juice, consists of heating the juice to 145-160°F for 5-30 seconds. It results in inactivation of pectinesterase and in reduction of the microbial flora. Heat treating steps are severely controlled in attempting to minimize the loss of fresh flavor.

In some processes, the juice is depulped prior to evaporation. After being preheated to 80°C in a plate preheater, the amount of pulp is reduced from 10% to 1-2% by centrifugation. The juice is then cooled down to 50-60°C in a heat exchanger.

Step 7: The juice is preheated by flowing through a heat exchanger before reaching the evaporator.

Step 8: Concentration of the juice is achieved by evaporation, which is done under vacuum and at the lowest temperature possible to avoid the development of a cooked flavor. Evaporation results in unavoidable loss of flavor. The juice is concentrated past (55° - Brix) to the commercial concentration level (42° - Brix).

To solve the problem of loss of flavor volatiles during the evaporation, several industrial alternatives have been considered.

Some recovery processes (e.g. distillation) of the flavor from the first stage of the evaporation are commercially used. The resulting flavor essence can be added back to the final product.

Concentration can be achieved by other means than evaporation, such as freeze concentration, reverse osmosis or filtration through selective membranes, which are low temperature processes. In these cases there is no heat-induced enzymatic inactivation.

Freeze concentration can be achieved in various ways. The juice can be passed through a scraped surface heat exchanger, or frozen by direct contact with a cryogenic liquid such as liquid nitrogen. Separation of the ice from the orange slurry is done by centrifugation or column washing to yield the concentrate. Freeze concentration causes a problem of solids loss.

Step 9: To counterbalance the loss in flavor, a determined percentage of fresh untreated juice is added to the overconcentrated juice. The final product has a percentage of solid concentrate of 42% (42° - Brix) and a flavor closer to that of fresh orange juice.

Step 10: The concentrate is transformed to a slush by passing it through a chilled scraped surface heat exchanger. It is then frozen solid after being packaged into containers (e.g., cans, or drums for further industrial use).

Step 11: The by-products of this process (50% of the orange) are the dried peel (animal feed), citrus molasses (concentrated waste water), oil (flavor chemical), citrus flour (dried pulp, albedo, core, membranes).

Further Processing: Citrus Fruit Juice Reconstituted from Concentrate

The water used for the reconstitution from the orange or other citrus concentrate is treated by passing through a ressurizing group, a dechlorination filter, and a sterilizing station.

Sugar is weighed, melted in a sugar melting tank, and passed through a syrup filter.

Concentrate is pumped, weighed, and mixed in the appropriate ratio with the syrup in mixing tanks.

The reconstituted fruit juice is then pasteurized through a heat exchanger, packaged and cooled down in a cooling tunnel.

The orange or other citrus juice is packaged and cooled down after step 6 of the above described Concentrate Production Process.

The present invention thus provides many advantageous aspects, some of which may be noted.

First processing and storage of orange or other citrus juice under any of the noble gases argon, xenon, krypton, neon, alone or in mixtures, or admixed with nitrogen or small amounts of oxygen or CO_2 or N_2 or He, greatly, and surprisingly, improve the retardation of oxidation as compared to that obtainable using nitrogen.

Second contacting the fruit or juice at any of the processing steps of peeling, extraction, pressing, separation, pumping, blending, holding storage, depulping, pasteurization, heating, evaporating, concentrating, freeze-concentrating, reblending, aroma recovery, reconstitution, or further processing, with noble gases greatly improves the flavor and fragrance, appearance, color, and quality of the intermediate and final products.

This improvement is demonstrated at a wide range of temperatures, including during heating or pasteurization, refrigeration, and freezing, including cryogenic freezing, and is effective under low or very high pressures.

Additionally, the noble gases, preferably argon, are more effective than nitrogen or carbon dioxide, and the effect is directly proportional to the degree of saturation of the product with noble gas.

Having generally described the present invention, reference will now be made to certain examples which are provided solely for purposes of illustration and which are not intended to be limitative.

EXAMPLE I

Several varieties of orange or other citrus juice including fresh squeezed, reconstituted from concentrate, and pasteurized versions of these, were subjected to GC/MS analysis of headspace after being stored variously under Ar, Xe, Kr, Ne, He, N_2, CO_2, N_2O, O_2, Air, and decile binary and ternary combinations of these gases.

Figure 38 illustrates a GC/MS of orange juice aroma volatiles under argon. The various parameters applicable are recited on Figure 38.

Figure 39 illustrates a GC/MS of orange juice aroma volatiles under nitrogen. The various parameters applicable are recited on Figure 39.

Figure 40 illustrates a GC/MS of orange juice aroma volatiles under oxygen. The various parameters applicable are recited on Figure 40.

From a comparison of Figures 38, 39 and 40, the damaging effect of oxygen may be seen, whereas the surprisingly superior effect of argon as compared to nitrogen may be seen.

Marked are the cyclohexanetetrol and tridecane peaks around 1853 seconds, which are well preserved in argon, much oxidized in nitrogen and very much oxidized in oxygen (also present is considerable siloxane column bleed).

For example, the glycosides present in the argon sample which produce peaks at 1570-1596 seconds are oxidized and not present at all in the oxygen sample, and present in trace quantities in the nitrogen sample. The same progressive oxidation differences are observed for the nitrile at 870 secs, the acid esters at 1040 secs, the pyrans at 1149 secs, the substituted cyclohexanone at 1217 secs, the substituted propanol at 1378 secs, and the substituted cyclohexane at 1490 secs (identifications tentative from NBS data library).

A sum of differences method was used to average quantitative improvement across many compounds, and it was observed that, generally, a 25-30% improvement in shelf life can be easily obtained using argon, for example, in accordance with the present invention.

In order to further illustrate the effect of the present invention, the various gases and gas mixtures as noted in Tables I and II were used as storage gases for orange juice.

In the following two tables, the color of the orange juice was measured by uv/vis spectrophotometer methodology, the flavor and aroma by GC/MS method and shelf life by GC/MJ methodology. The relative progress of oxidation over time using the gases and gas mixtures of the present invention was compared with air, oxygen or nitrogen storage.

An organoleptic/sensory panel of five persons tasted through blind samples the color, flavor and aroma which are congruent with and contain the above instrumental measurements. Tables I and II follow:

Table I

Orange Juice Evaluation Effect of different gas storage atmosphere		
Gas Mixes	Color	Flavor Aroma
N_2	64	60
Ar	92	93
Ar:Kr 9:1	95	96
Ar:Ne 9:1	93	92
Ar:Xe 9:1	100	100
Ar:Xe 99:1	99	98
He	65	63
Ne	85	87
Kr	93	94
Xe	100	100
Air	20	35
O_2	0	0
N_2:O_2 9:1	30	35
Ar:O_2 9:1	85	90
CO_2	30	55
N_2:CO_2 8:2	30	45
Ar:CO_2 8:2	50	70
Relative scaling of effect compared to oxygen, set to 0		

Table II

Orange Juice Gas Mixtures in decile combination trials, as:		
Gas Mixtures	Color	Flavor Aroma
$Ar:N_2$		
100:0	92	93
80:20	86	88
50:50	77	79
20:80	68	72
Ar:He		
100:0	92	93
80:20	87	88
50:50	75	76
20:80	66	71
$N_2:O_2$		
100:0	64	60
90:10	30	35
80:20	20	20
70:30	0	0
$Ar:O_2$		
100:0	92	93
90:10	85	90
80:20	70	78
70:30	60	65
Ar:Kr:Xe		
60:20:20	100	
Relative scaling of effect compared to oxygen, set to 0		

As used herein, the term "substantially" generally means at least 75%, preferrably at least about 90%, and more

preferably about 95%. This refers not only to duration of storage but also the volume of the containing means.

The present invention will now be further illustrated by reference to certain examples which are provided solely for purposes of illustration and are not intended to be limitative.

Example 2

Several varieties of orange juice including fresh squeezed, reconstituted from concentrate, and pasteurized versions of these, were subjected to GC/MS analysis of headspace after being stored variously under Ar, Xe, Kr, Ne He, N_2, CO_2, N_2O, O_2, Air, and decile binary and ternary combinations of these gases for days.

Similar studies were conducted on several varieties of beer and ale. Beer was also studied by ultraviolet/visible spectrophotometry.

Edible oils, including vegetable oils, corn oils, soybean oils, and olive oils were studied by high performance liquid chromatography.

Figure 1 shows UV/VIS spectra of beer oxidation after 30 days storage under gas, and clearly demonstrates the improved retardation of oxidation of beer under argon versus that under nitrogen. The retardation is 35% overall for up to 2 years.

Figures 2-4 show GC/MS of beer under Ar, N_2 and O_2, respectively. It can readily be determined from these figures that beer volatiles degrade more rapidly under nitrogen than under argon due to oxidation.

For example, the peak at 1115 seconds is an oxidation product which increases relative to the peak at 1234 seconds during oxidation. The ratio shows oxidation under $O_2>N_2>Ar$, the improvement due to argon being about 25% after 30 days relative to N_2. Other examples of this improvement are found in peaks at 750, 1190, 1225, 1520, 1840, 1890, 1933, and 2360 seconds.

A National Bureau of Standards (NBS) Library Search supports the identification of the above peaks as corresponding to an imidazole, a substituted bicloactane, a substituted tridecane, an alcohol, possibly pentadecanol, cyclohexane tetrol, a tetradecane diol, a glycoside and a substituted benzoic acid, respectively.

Figures 5-7 show GC/MS of orange juice aroma volatiles under Ar, Figures 8-10 N_2, and Figures 11-13 O_2, respectively. It can be seen by comparison of the peaks from these figures that oxidation is better retarded by Ar than by N_2.

Marked are the cyclohexane tetrol and tridecane peaks around 1853 seconds, which are well preserved in argon, much oxidized in nitrogen and very much oxidized in oxygen (also present is considerable siloxane column bleed).

For example, the glycosides present in the argon sample which produce peaks at 1570-1596 seconds are oxidized and not present at all in the oxygen sample, and present in trace quantities in the nitrogen sample. The same progressive oxidation differences are observed for the nitrile at 870 secs, the acid esters at 1040 secs, the pyrans at 1149 secs, the substituted cyclohexanone at 1217

secs, the substituted propanol at 1378 secs, and the substituted cyclohexane at 1490 secs (identifications tentative from NBS data library).

A sum of differences method was used to average quantitative improvement across many compounds, and it was found that generally a 25-30% improvement in shelf life can be obtained easily using argon.

Oxidation of olive oils and other edible oils was consistently retarded by 30% or more when stored under argon or other noble gas containing mixtures as measured by % change by weight of original oil constituents to oxidized forms by HPLC or TLC. Precise compositional analysis of triglycerides and lipids was obtained causing phenyl methyl silicone GC/MS.

Figure 1 illustrates a UV/VIS spectra of beer oxidation after 30 days storage under different gases as indicated.

Figure 2 illustrates a GC/MS chromatogram plot of beer volatiles after 30 days storage under argon.

Figure 3 illustrates a GC/MS chromatogram plot of beer volatiles after 30 days storage under nitrogen.

Figure 4 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 5 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 6 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 7 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 8 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 9 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 10 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under nitrogen.

Figure 11 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under oxygen.

Figure 12 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under oxygen.

Figure 13 illustrates a GC/MS c.p. of orange juice aroma volatiles after 30 days storage under argon.

Figure 14 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 15 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 16 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 17 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 18 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 19 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 20 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under oxygen.

Figure 21 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 22 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 23 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 24 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 25 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 26 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 27 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under nitrogen.

Figure 28 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 29 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 30 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 31 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 32 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 33 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 34 illustrates a GC/MS c.p. of beer volatiles after 30 days storage under argon.

Figure 35 is a schematic illustration of a process for manufacturing soybean oil from soybeans.

Figure 36 is a schematic illustration of a process for manufacturing refined salad oil or refined margarine or shrotening oil from crude soybean oil.

Figure 37 is a schematic illustration of a production process of orange juice from oranges.

Figure 38 illustrates a GC/MS of oragne juice aroma volatiles under argon.

Figure 39 illustrates a GC/MS of orange juice aroma volatiles under nitrogen.

Figure 40 illustrates a GC/MS of orange juice aroma volatiles under oxygen.

Generally, in accordance with the present invention, beverages such as beer, ale, stout, soft drinks, such as all colas and citrus juices, such as all orange juice may be preserved.

Illustrative, but non-limitative examples of citrus or other juices include orange juice, lemon juice, lime juice, pineapple juice and apple juice.

Further, it is understood that the effect of the present invention may be obtained by using the gases, gas mixtures, liquids or liquid mixtures of the present invention through all stages of processing or storage of the beverages or edible oils or during any one stage or portion thereof.

II. USE OF THE PRESENT INVENTION IN PRESERVING THE AROMA AND FRESHNESS OF EDIBLE OILS

In accordance with another aspect of the present invention, it has been unexpectedly discovered that if

instead of solely blanketing the headspace above a seed oil which is stored in a tank or a bottle with any kind of inert gas, a gas containing an element selected from the group consisting of argon, krypton, xenon, neon and a mixture thereof, is sparged into the seed oil and/or precursor constituent thereof or injected above the seed oil and/or precursor constituent thereof in order to saturate or substantially saturate the seed oil and/or precursor constituent thereof with the gas or gas mixture, the color and/or the flavor and/or the aroma and/or the shelf life of the the seed oil and/or precursor constituent thereof, may be preserved or improved particularly when the saturation or substantial saturation is maintained throughout the volume of the storage container and during substantially all the time that the said seed oil and/or precursor substituent thereof is stored in said container. The term "substantially saturate" means that it is believed to be necessary to completely and/or constantly saturate the wine with seed oil and/or precursor substituent thereof with the gas or gas mixture (i.e., having the maximum amount of gas solubilized in the seed oil and/or precursor). Usually, the seed oil and/or precursor is saturated to more than 50% of its (full) saturation level and preferably more than 70%, while 80% or more is considered the most adequate level of saturation of the seed oil and/or precursor. Of course, supersaturation is also possible. This means that if during the storage life of the seed oil and/or precursor in the container, the seed oil and/or precursor is not saturated with noble gas at least from time to time or even quite

longer, as long as it remains generally substantially saturated, the results of the present invention are usually obtained. While it is believed that it is important that the entire volume of the container be saturated or substantially saturated with one of the above gas or a mixture thereof, it is quite possible to obtain the results according to the invention if a part of the volume is not saturated during preferably a limited period of time or is less saturated or substantially saturated than other portions of the volume of the seed oil and/or precursor in the container.

As used herein, the term "noble gas" means Kr, Ar, Ne, or Xe. He is not used as it does not work, and Rn is radioactive and not useful.

As used herein, the term "precursor" refers to the natural seed oil source or any crude preliminary or intermediate product which is obtained prior to a final seed oil product. For example, the term "precursor" may refer to raw soybeans, cracked or dehulled soybeans, crude soybean oil, degummed oil, neutralized oil or bleached oil, for example. Any of these products may benefit from the present invention.

Further, for seed oils which are odorless and/or tasteless, these qualities may be more readily preserved. For seed oils which have a characterizable odor and/or taste, these qualities are also more readily preserved and improved in the sense that they hold up better over time in storage than would otherwise be the case.

While at least one of the above gases must be present in order to obtain the benefits of the invention, said gases can be diluted with some other gases, in order to keep for example the invention economically valuable. Said diluent gases are preferably selected from the group comprising nitrogen, oxygen, nitrous oxide, air, helium or carbon dioxide. In case of an oxygen-containing gas or another reactive gas such as carbon dioxide, their degradative properties are such that these properties will mask the effect of noble gases, certainly in mixtures where they comprise 50% vol. or more and possibly 30% vol. or more. When those mixes comprise 0% to 10% vol. of these other gases, the noble gases referred to above are still extremely effective, while between 10% vol. and 20% vol. they are usually still effective, depending on the type of gases and conditions, which might be easily determined by the man skilled in the art.

In case of nitrogen and/or helium gas, the effect of noble gases consisting of Ar, Ne, Kr, Xe in the mixture is linearly proportional to its concentration in the mixture, which evidences that nitrogen and/or helium have no effect on substantially preventing oxidation of seed oil and/or precursors thereof. The mixture of noble gas and nitrogen and/or helium can thus comprise any amount (% volume) of nitrogen and/or helium: however, in practice, the lesser the proportion of noble gas selected from the group consisting of Ar, Ne, Kr and Xe, the larger the time required to achieve saturation or substantial saturation of the seed oil and/or precursor.

Among the active gases (Ar, Kr, Xe, and Ne), it is preferred to use argon because it is cheaper than the other active gases. However, mixtures of argon and/or krypton and/or xenon are at least as effective as argon alone. It has also been unexpectedly found that mixtures comprising between 90 to 99% vol. argon and 1 to 10% Xe and/or Kr are usually the most effective as exemplified in the further examples (whether or not they are diluted with nitrogen, helium, or nitrous oxide). The difference in effect between the active gases defined hereabove and nitrogen have been also evidenced by the fact that mixtures of argon and oxygen or carbon dioxide have a similar (while decreased) effect than argon alone, while nitrogen mixed with oxygen or carbon dioxide evidenced no protective or preservative effect compared to oxygen or carbon dioxide alone.

It is believed that the saturation or substantial saturation of the wine is an essential feature of the invention and that no one in the prior art has ever disclosed nor suggested said feature.

Generally speaking, Xe is the most efficient gas according to the invention, followed by Kr, Ar and Ne. Among the suitable mixes, either pure or diluted with N_2, He, N_2O (or even air, oxygen or a small amount of hydrogen) are the Ne/He mix comprising about 50% vol. of each, and the Kr/Xe mix comprising about 5-10% vol. Xe and about 90-95% vol. Kr, with a small amount of argon and/or oxygen (less than 2% vol.) or nitrogen (less than 1% vol.).

The temperatures at which the invention is carried out is usually between about 0°C to 60°C, and preferably about 10°C and 30°C.

The injection of the gas or gas mixture into the seed oil and/or precursor and/or into the container, e.g. by sparging is usually done at about 1 atmosphere but is still quite operable at 2 or 3 atmospheres, while saturation is increased at higher pressures. The pressure of the gas above the seed oil and/or precursor in the container shall be, in any case, preferably lower than 10 atmospheres and it is usually acceptable to maintain it lower than 3 atmospheres.

Saturation or substantial saturation of the seed oil and/or precursor can be measured by various methods well-known by the man skilled in the art, including but not limited to thermogravimetric analysis or mass change weighing.

There are a variety of standard methods available for the detection, qualitative and quantitative measurement of gases, and several are especially well suited for the determination of degree of saturation of noble gases into liquid samples.

Samples generally are completely evacuated as a control for zero % saturation. Such samples may then be completely saturated by contact with noble gases such that no additional noble gas will disappear from a reservoir in contact with the sample. Such saturated samples may then have their gas content driven off by trapped evacuation or by increase in temperature, and said gas sample identified

quantitatively and qualitatively. Analysis is of trapped gases, reservoir gases, or some other headspace of gases, not directly of the sample.

Direct sample analysis methods are available, and include comprehensive GC/MS analysis, or by mass or thermal conductance or GC analysis and comparison with calibrated standards.

The simplest method is GC/MS (gas chromatography/mass spectrometry), which directly determines gas compositions. By preparing a standard absorption curve into a given sample for a series of gases and mixtures, one can accurately determine the degree of saturation at any point in time.

GC/MS is applied to the gas itself, as in the headspace above a sample. The technique may be used either to determine the composition and quantity of gas or mixture being released from a sample, or conversely the composition and quantity of a gas or mixture being absorbed by a sample by following the disappearance of the gas.

Appropriate GC/MS methods include, for example, the use of a 5 Angstrom porous layer open tubular molecular sieve capillary glass column of 0.32 mm diameter and 25 meter length to achieve separation, isothermally e.g. at 75°C or with any of several temperature ramping programs optimized for a given gas or mixture e.g. from 35-250°C, wherein ultra-high purity helium or hydrogen carrier gas is used at e.g. 1.0 cc/min flow rate, and gases are detected based upon their ionicity and quantitative presence in the sample, and characterized by their unique mass spectra.

Appropriate experimental conditions might include, for example, completely evacuating a given sample under vacuum to remove all absorbed and dissolved gases, then adding a gas or mixture to the sample and measuring a) the rate of uptake of each component as disappearance from the added gas, and/or b) the final composition of the gas headspace after equilibration. Both measurements are made by GC/MS, and either method can be used in both batch and continuous modes of operation.

A simplification of this analysis entails the use of a GC only, with a thermal conductivity detector, wherein adequate knowledge of the gas saturation process and preparation of calibration curves have been made such that quantification and characterization of gases and mixtures can be accomplished without mass spectral analysis. Such instruments are relatively inexpensive and portable.

A further simplification would depend solely upon measurement of the mass change in the sample upon uptake of various gases or mixtures, which depends upon the use of standard curves or absorption data available from the literature.

An alternate method for such mass measurements is thermogravimetric analysis, which is highly precise, wherein a sample is saturated with gas and mass changes are correlated to thermal change.

Contacting oils during their elaboration and manufacture in processes designed to produce oil from seeds or kernels with noble gases significantly retards oxidation and improves the quality of the oils obtained. The more

complete the contact between the noble gases and the oil in process, and the longer the duration of the contact, the better the improvement. The improvement is best when the ratio of molecules of gas to units of oil is maximized. Significant improvement is observed when the liquid oil is saturated with noble gases under optimal process operating conditions. Specifically, by increasing pressure, lowering temperature, enhancing mixing, or employing other means to maximize gas-oil contact the improvement may be enhanced.

Generally, it has now been discovered that noble gases, particularly argon, possess an inherent molecular ability to repress oxidation however initiated, whether by molecular oxygen in solution or from donated oxygen. Further, that this effect is strong even in the presence of oxygen, up to certain limits depending upon process conditions. In any event, it is always significant when noble gas is added to current processes by sparging, blanketing, or under pressure so as to achieve substantial saturation.

In placing noble gases, preferably argon, in contact with seed oils during the seed oil manufacturing process, the rates and yields of degradative oxidative reactions may be significantly lowered and the quality of the final product is significantly improved. Moreover, the optimal result is obtained when seed oil and/or precursors thereof is completely saturated with noble gases at every stage of the manufacturing process. Specifically, noble gases are saturated into the oil at each of the following stages:

Grinding/Cracking, Dehulling, Flaking, Extraction, Degumming, Alkali Refining, Bleaching, Hydrogenation, Deoderization, Winterization; and at any step involving Pressing, Filtering, Desolvation, Clarification, Transfer into storage/holding or transport vessels, or Storage.

Generally, the present invention may be used advantageously with any single manufacturing step, series of manufacturing steps or all steps in the production of seed oils, the refining of vegetable oils or in the production of refined oil products.

For example, the essential elements or stages of a typical seed oil production process, i.e., a soybean oil production process, may be described as follows:

Step 1: Unloading system for trucks

Step 2: Storage facilities and drying, cleaning, tempering, classification of soybeans.

Step 3: As preparation of soybeans for extraction, the beans are cracked to loosen the hulls from the soybean meats and assist in the flaking operation. Corrugated rollers are used for the cracking operation. Dehulling or separation of the hull material from the cracked meats is necessary to increase extraction efficiencies. Dehulling is performed by a combination of air aspiration, screening, centrifugal separation, and density separation methods.

Flaking the cracked, dehulled soybean meats facilitates the extraction process by disruption of the internal cellular structure of the bean and by allowing better contact of the extracting solvent with the internal parts of the seed. Flaking is done by heating and steaming the

cracked meats and passing them through differential roller mills.

Step 4: Oil is extracted from the flaked beans in a continuous countercurrent percolation extractor, using hexane as solvent. The solution of oil in solvent, called rich micella, is then pumped to a solvent recovery system, in which the solvent is removed leaving solvent-free crude oil in the liquid phase. The solvent is kept near 120°F (50°C) during extraction to speed the solubilization of oil from the flakes. The micella is then separated from the flakes and distilled for recovery of the crude soybean oil. The solvent is recovered for further use. The crude soybean oil is then pumped to storage tanks for further processing.

Step 5: Degumming of the crude oil, including lecithin, and oil drying and cooling is accomplished by mixing the crude oil with a certain percentage of hot water to flocculate the phosphatides, which are subsequently removed in a centrifuge; the oil is then dried and cooled, and pumped into the crude oil storage tank. The separated lecithin sludge is dried under vacuum and mild heat treatment, then cooled and filled into cans or drums.

Further processing steps which may be used are as follows.

Further Processing: Phospholipids, or lecithin, present in the crude soybean oil will precipitate during storage and contribute to deterioration during use of the oil. The degumming process involves the addition of a small amount of water or steam to the crude oil, resulting in the hydration of the phospholipids and their subsequent precipitation.

Acidic catalysts are sometimes added with the water to improve the hydration. The precipitated phospholipids are then separated by centrifugation and are vacuum-dried.

Step 6: Alkali refining is carried out to remove free fatty acids which decrease the heat stability of the oil. The degummed soybean oil is alkali-refined to remove the free fatty acids, residual phospholipids, and color from the oil. Alkali refining consists of addition of caustic soda, soda ash, or a combination of the two to neutralize the free fatty acids present. Careful addition of the alkali is required to prevent further degradation of the oil. The neutralized free fatty acids or soaps are removed from the oil by centrifugation or settling. The alkali refined oil is further washed with water to remove all traces or alkali and soaps present and then dried.

Step 7: Bleaching (decolorizing) removes the color bodies or pigments present in the oil by adsorption on activated earth or carbon. The bleaching agent is simply dispersed in the oil and removed by filtration. The bleached oil is sent to the hydrogenation unit or to the deodorizers, depending upon the final use. Food requiring improved oxidative stability or plastic fats such as margarines or bakery shortenings require hydrogenation.

Step 8: Hydrogenation of vegetable oils permits the substitution of vegetable oils for animal-derived fats and the substitution of the various types of vegetable oils with soybean oil. Hydrogenation is performed by purging the oil with hydrogen gas at an elevated temperature and pressure in the presence of a catalyst. Nickel catalysts are generally

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used. The addition of hydrogen to the fat saturates the molecular structure. The degree of saturation depends upon the time, temperature, and pressure of hydrogenation.

Step 9: Deodorization of the oil removes the undesirable flavor and odor constituents. Oils must be odorless and bland in flavor in order to be suitable for food use. Deodorization is carried out under high temperature and vacuum with steam to assist volatization of the undesirable components.

Step 10: Winterization is performed on lightly hydrogenated soybean oil that is to be used as a salad oil. The oil, in addition to conforming to oxidative stability requirements, must remain clear at refrigerator temperatures. Winterization consists of cooling of the oil and filtering off the cloudy haze that forms.

Step 11: Refined soybean oil is a highly unsaturated oil and will develop, after storage, characteristic flavors and odors described as painty or fishy. The development of these flavors is called reversion, and is a result of the oxidation of the linolenic and other acid components of the oil. Exposure of the oil to air during processing and controlled hydrogenation to partially saturate the linolenic acid increases the tendency of soybean oil to reversion. Metal sequestrants, such as citric acid, are sometimes added during deodorization to inactivate the prooxidant metals such as iron and copper. Antioxidants may also be added.

The following steps generally describe a typical process for refining vegetable oils.

Refining of Vegetable Oil

Step 1: Crude oil (e.g., peanut, soybean, sunflower, corn, cotton-seed, etc.) is pumped into outside storage tanks.

Step 2: Caustic refining is accomplished by transferring the oil from storage tanks to a day tank which feeds the neutralizing section, where the free fatty acids in the oil are neutralized by the addition and mixing of caustic soda under controlled conditions. The neutralized fatty acids (soapstock) are phosphoric acid treatment may be used to first remove any gums in the oil. The oil is then washed to remove remaining soap, followed by vacuum drying.

Step 3: Bleaching is carried out by the addition of bleaching earth under vacuum. The light-colored bleached oil is then filtered and delivered to a buffer tank which serves the deodorizing section, the next step in the process.

Step 4: The deodorizing step is carried out in a deodorizer operating at an absolute pressure of 2-6 mm Hg and at temperatures of 220 to 275°C, in which stripping steam is passed through the oil. The process is semi-continuous. The deodorized oil is then partially cooled and given a "polishing filtration", after which it is cooled further.

Step 5: Filling of refined, bleached and deodorized cooking oil is carried out at the terminus of the process.

Figures 1 and 2 will now be explained in more detail.

Figure 1 illustrates the production of crude soybean oil from soybeans. First, soybeans are received, dried, cleaned and stored. Then, the soybeans are cracked on a corrugated roller will, for example. Thereafter, the cracked soybeans are dehulled and flaked to produce soy flakes, which are then subjected to solvent extraction using a continuous countercurrent percolation extractor. After solvent recovery in a stripper crude soybean oil is collected.

In Figure 1, a solvent condenser is shown for hexane in fluid correction with the extractor. The condenser typically uses water.

Figure 2 illustrates the production of wither refined salad oil or refined margarine or shortening oil. First, crude soybean oil is degummed using water/steam to remove lecithin and to afford a degummed oil. The degummed oil is then alkali refined with caustic soda to form soaps and to afford a neutralized oil, which is bleached with activated carbon or earth to form cake and bleached oil. The bleached oil is hydrogenated and deodorized with some variation as shown in Figure 2 to produce either refined salad oil or refined margarine or shortening oil.

Generally, in accordance with the present invention, any of the noble gases, xenon, krypton, argon, or neon significantly inhibit oxidative processes during the manufacture of seed and other vegetable oils. Helium has essentially no effect primarily due to its lower solubility and tendency to escape from present process equipment. However, it may be used as a carrier gas. Further, these

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gases have a significant beneficial effect when they are applied to any portion or stage of the manufacturing process during which oxidation normally occurs.

Although significant benefits are found when the application is made at each of several process steps, jointly or severally, including all of those listed above, it is preferred that the present invention is used in conjunction with at least two process steps, and even more preferred if used in conjunction with all process steps.

While any of the noble gases may be used, the preferred noble gas to use is argon because of its adequate solubility and inherent molecular properties which result in excellent beneficial effect, and because of its lower cost. Moreover, application of the argon can be made, and has been made in our pilots, by sparging, pressurized superimposition, pressure treatment, cryogenic introduction, vacuum treatment followed by gas introduction, temperature swing of oil such that a degassed hot oil stream or pool is cooled with concomitant introduction of gas, blanketing, introduction into shrouded equipment, or by other means.

Mixtures of argon with other noble gases except helium are notably more effective only under special circumstances wherein complete saturation with argon through a large portion of the process is not feasible nor desirable. For example, high-value specialty oils are better finished and/or stored under noble gas mixtures containing Krypton or Xenon from 0.1-100% in Argon. The use of argon alone for low-value high-volume production processes, such as for corn and soybean oils, is entirely adequate.

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Further, the noble gases remain effective in the presence of oxygen within limits. The effectiveness of the noble gases is still significant between 0.001 and 5% oxygen content measured as percent of saturation in solution, as well as 0.001-5% measured as percent in resultant application atmosphere. From 5-10% oxygen content, measured as atmospheric, significance declines markedly, but under process conditions measurable improvements may be observed with care. From 10-20%, the effect gradually disappears, until at 30% no effect is seen. In solutions with oxygen contents between 5 and 100% of saturation, significant effects of noble gases can be measured, though they decline over that range.

Additionally, the present invention is effective for all oil seed and vegetable products obtained by extraction or pressing.

Also, as used herein, the term "noble gas" is intended to include argon, xenon, krypton and neon. Helium may be used although it is not preferred due to its ease of escape. Radon is not used as it is dangerously radioactive.

In accordance with the present invention, argon, xenon, krypton and neon may be used alone or in any combination. For example, binary mixtures of argon-xenon, krypton-xenon or xenon-neon may be used, or ternary mixtures of argon-xenon-krypton may be used, for example.

As noted above, a simple noble gas or mixture of noble gases may be used. However, mixtures containing at least one noble gas with one or more other carrier gases may also

be used. Carrier gases may include, for example, nitrogen, carbon dioxide, nitrous oxide and helium or even oxygen at sufficiently low concentrations.

Generally, the effect of the present invention may be obtained at a range of pressures form about near-vacuum, i.e. about 10^{-8} torr, to about 100 atmospheres. However, it is generally preferred that a pressure be used between about 0.001 to about 3 atmospheres. Further, a range of temperature is generally used which is the same as the operable and preferred temperatures of storage for beverages and edible oils and for different stages of processing. For example, such temperatures may range from freezing temperatures to cooking temperatures. However, lower temperatures and ambient temperatures are generally used for storage.

As noted above, a single noble gas, such as argon, or a mixture of noble gases may be used in accordance with the present invention. However, mixtures containing at least one noble gas and one or more carrier gases may also be used.

For example, in accordance with the present invention it is advantageous to use inexpensive production plant off stream gases having a composition of about 90%kr and 10% Xe in volume % based on the total gas volume or Ne:He 1:1.

It is also advantageous to use mixture containing an effective amount of one or more noble gases in deoxygenated air. Generally, as used herein, the term "deoxygenated air"

is intended to mean air having generally less than 15 volume % or 10 volume %, preferably less than 5 volume % oxygen therein.

Further, the gas or gas mixtures of the present invention may be used as gases or may also be introduced in the beverage or edible oil or into the headspace or even above in storage means in order to form the described atmosphere.

Color improvement in the oils is dramatic and represents, by itself, a very surprising and significant improvement, wherein less coloration is often desirable and A.O.C.S. standard optimal color guidelines are more easily met.

Flavor is also improved according to a blind taste test of the oils, wherein it is generally desirable that oils, such as soybean oils have no taste whatsoever.

As in the application jointly deposited, storage of any liquid foodstuff or beverage under any of the noble gases argon, xenon, krypton, neon, or helium, alone or in mixtures, or admixed with nitrogen or small amounts of oxygen or carbon dioxide or nitrous oxide greatly improve the retardation of oxidation as compared to that obtainable using nitrogen.

Notably, the effect of the present invention is demonstrated over a wide range of temperatures, including during cooking or pasteurization, refrigeration, and freezing, including cryogenic freezing. It is also observed under low or very high pressures.

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The present invention will now be further illustrated by reference to certain examples which are provided solely for purposes of illustration and are not intended to be limitative.

Example 3

Seed oils were prepared from soybeans, corn, flaxseed, sunflower, safflower, rapeseed (or canda), cottonseed and peanut in the laboratory. Additionally, certain aspects of the manufacturing process were assayed using tung oil, chaulmoogra oil, castor oil, olive oil all acquired both as seed and oil, and commercial samples of many different seed and vegetable oils. The aspects studied included storage, heating, pressure, addition or oxygen, and transport during process steps.

Two example processes were assayed most carefully; corn oil processing and soybean oil processing. Every step of each was modeled in the laboratory such that a small laboratory-scale pilot plant was effected, wherein oil was obtained from corn kernels and soybeans in a manner entirely similar to that of a full-scale manufacturing plant.

Evaluation of oil quality was performed according to the "Official Recommended Practices of the American Oil Chemists' Society, Fourth Edition, with 1991 Supplements". Tests conducted included:

Peroxide Value

Color

Retractive Index

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Fat Stability (active O_2)

Anisidine Value

Free Fatty Acids

Accelerated Oxidation

Additional tests were conducted, including:

Taste Panel (Standard Sensory Panel for Aroma (fragrance) and flavor).

Spectrophotometric time-drive tracking of color change over time

Gas chromatograph/mass spectrometer analysis of flavor and fragrance components

Fatty acid analysis by gc/ms, high performance liquid chromatography (HPLC) and thin layer chromatography (TLC)

All tests were conducted using oils processed and stored under each of the following atmospheres:

1. air
2. oxygen
3. nitrogen
4. carbon dioxide
5. argon
6. neon
7. krypton
8. xenon
9. helium

Additionally, tests were carried out using mixtures of noble gases, for example binary and ternary mixtures of noble gases (e.g., 90:10 Ar:Xe, 90:10 (90:10 Ar:Xe):(Ne)) in many combinations for at least one type of oil each.

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Additionally, tests were carried out using gases 3-9 from the list above or many combinations of those gases, to which was added oxygen from 0.001, 0.01, 0.1, 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, 25.0, 50.0, and 90.0 percent final composition.

Additionally, a range of pressures from very near vacuum to 100 atmospheres was used.

Additionally, a wide range of process temperatures was used, from colder-than-process (below the freezing point of samples, -200°C in extreme) to hotter-than-process (above the point of complete thermal decomposition of the samples, +1000°C in extreme).

Additionally, a wide range of physical parameters were assayed and manipulated in individual experiments, including pH, Temperature, Pressure, salt and ion concentrations, water content, age of sample, duration of treatment, protein content, and physical shearing of samples.

The best results obtained for the following tests and oil pairs are given as % fully oxidized (oxygen saturated sample). Results were similar for samples taken during process and 30, 60, 90 and 120 days after storage when corrected for degree of oxidation of oxygen samples. As oxidation is an ongoing process, greater improvement was noted for longer storage times.

Test:

1. Peroxide Value <1.0 mEq/kg = unoxidized, 10 = oxidized
2. Fat Stability (active O_2)
3. Anisidine Value <2.0 = unoxidized
4. Color

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5. GC/MS Aroma

6. Free Fatty Acids 0.05 = unoxidized

Gas used in process:

1. Oxygen
2. Air
3. Nitrogen
4. CO_2
5. Argon
6. Neon
7. Krypton
8. Xenon
9. Helium

Treatment Soybean Oil

	PV	FS	AV	Color	GC/MS	FFA
Gas O_2	%100	%100	%100	%100	%100	%100
Air	99	99	99	97	98	95
CO_2	99	100	95	125	130	99
N_2	95	98	96	96	97	95
Ar	76	72	74	68	70	75
Ne	81	82	79	73	78	84
Kr	74	70	69	59	70	77
Xe	69	71	73	70	65	77
He	94	89	95	94	93	91

In all cases, results of mixtures of Xe, Kr, or Ne with Ar showed slight improvement over Ar alone. In all cases, addition of O_2 to Ar, Ne Kr, or Xe lessened the effect in an approximately linear amount directly related to oxygen

concentration of 5% or more measured as above, but in a more exponential manner in the range of 0.001-5%.

Tests with each of the other oils yielded similar results when expressed as a percentage of maximum observed oxidation, but actual values were different for each.

Thus, the present invention generally provides a method of preserving seed oils or vegetable oils by contacting the same with the present gases in storage.

The present invention also provides a method of inhibiting both enzymatic and other oxidations in seed oils or vegetable oils by contacting the same with the present gases. By "other oxidations" is meant all forms of oxidation other than enzymatic which may occur. This oxidation may either be due to the presence of air or of any other internal oxygen donor in the oil.

As used herein, the term "substantially" generally means at least 75%, preferably at least about 90%. This refers to not only duration of storage but also the volume of the containing means.

Having described the present invention, it will now be apparent to one of ordinary skill in the art that many changes and modifications may be made without departing form the specification and the scope of the present invention.

CLAIMS

1. A method of improving the aroma and flavor of beverages or edible oils or both, which comprises contacting the same during at least a portion of processing and/or storage thereof with a noble gas, a mixture of noble gases or a gas mixture containing at least one noble gas and a carrier gas.

2. The method according to Claim 1, wherein said beverage is selected from the group consisting of citrus fruit juice, beer or vegetable oil.

3. The method according to Claims 1 or 2, wherein said noble gas is argon, neon, krypton and/or xenon.

4. The method according to one of Claims 1 to 3, wherein said mixture comprises at least one noble gas and deoxygenated air.

5. A method of improving a process of manufacturing a seed oil or vegetable oil or a precursor thereof according to one of Claims 1 to 4, which comprises injecting a gas or gas mixture into the seed oil or vegetable oil or precursor thereof in containing means, or into the containing means containing the same, the gas or gas mixture containing an element selected from the group consisting of argon, krypton, xenon and neon and a mixture thereof; substantially saturating the seed oil, vegetable oil or precursor thereof with said gas or gas mixture; and maintaining said saturation substantially throughout the volume of the seed oil, vegetable oil or precursor thereof or the containing means therefor and during substantially all of the duration

that the seed oil, vegetable oil or precursor is stored in the containing means.

6. A method of controlling oxidative degradation of a seed oil, vegetable oil or precursor thereof according to one of Claims 1 to 5, which comprises injecting a gas or gas mixture into the seed oil or vegetable oil or precursor thereof in containing means or into the containing means containing the same, the gas or gas mixture containing an element selected from the group consisting of argon, krypton, xenon and neon and a mixture thereof; substantially saturating the seed oil, vegetable oil or precursor thereof with said gas or gas mixture and maintaining said saturation substantially throughout the volume of the seed oil, vegetable oil or precursor thereof or the containing means therefor and during substantially all of the duration that the seed oil, vegetable oil or precursor is stored in the containing means.

7. A method of improving the aromas or the flavor or both of a citrus juice or precursor thereof according to one of Claims 1 to 4, comprising injecting a gas or gas mixture into the citrus juice or precursor thereof or both in containing means or into containing means therefor, the gas or gas mixture containing an element selected from the group consisting of argon, krypton, xenon, neon and a mixture thereof; substantially saturating the citrus juice or precursor thereof with said gas or gas mixture, maintaining said saturation substantially throughout the volume of the containing means and during substantially all the duration the citrus juice or precursor is stored in said container.

8. A method of improving a process for producing citrus juice according to one of Claims 1 to 4 or 7, comprising injecting a gas or gas mixture into the citrus juice or precursor thereof or both in containing means or into containing means thereof during the process for producing the citrus juice, the gas or gas mixture containing an element selected from the group consisting of argon, krypton, xenon and neon, and a mixture thereof; substantially saturating the citrus juice or precursor thereof with the gas or gas mixture; and maintaining the saturation substantially throughout the volume of the containing means and during substantially through the duration of the process by which the citrus juice is produced.

9. A method according to one of Claims 1 to 8, wherein said gas is injected in gaseous form or liquid form or both.

10. The method according to one of Claims 1 to 9, wherein said seed oil, vegetable oil, citrus juice, beer, or precursor is saturated to more than 50% volume of its full saturation level.

11. The method according to one of Claims 1 to 10, wherein said seed oil, vegetable oil, citrus juice, beer or precursor is saturated to more than 70% volume of its full saturation level.

12. The method according to one of Claims 1 to 11, wherein said seed oil, vegetable oil, citrus juice, beer or precursor is saturated to more than 80% volume of its full saturation level.

13. The method according to one of Claims 1 to 12,

wherein said carrier gas comprises a gas selected from the group comprising nitrogen, oxygen, nitrous oxide, air, helium, carbon dioxide or mixtures thereof.

14. The method according to one of Claims 1 to 13, wherein the gas mixture or the element of the gas mixture comprises about 90% to 99% volume argon and 1% to 10% volume Xe and/or Kr.

15. The method according to one of Claims 1 to 14, wherein the gas mixture or the element of the gas mixture comprises about 50% volume Ne and 50% volume He.

16. The method according to one of Claims 1 to 15, wherein the gas mixture or the element of the gas mixture comprises about 5% to 10% volume Xe and 90% to 95% volume Kr.

17. The method according to one of Claims 1 to 16, wherein the temperature is comprised between 0°C and 40°C.

18. The method according to one of Claims 1 to 16, wherein the temperature is comprised between 10°C and 30°C.

19. The method according to one of Claims 1 to 18, wherein the pressure is less than 10 atmosphere.

20. The method according to one of Claims 1 to 19, wherein the pressure is less than 3 atmosphere.

21. The method according to one of Claims 1 to 20, wherein the pressure is between 1 and 2 atmospheres.

22. The method according to one of Claims 1 to 21, wherein the pressure is about 1 atmosphere.

23. The method according to one of Claims 1 to 22, wherein said seed oil is selected from the group consisting of soybean oil, rapeseed oil, cottonseed oil, peanut oil,

tung oil, chaulmoogra oil, castor oil and olive oil, sunflower seed oil, safflower oil, corn oil and flaxseed oil.

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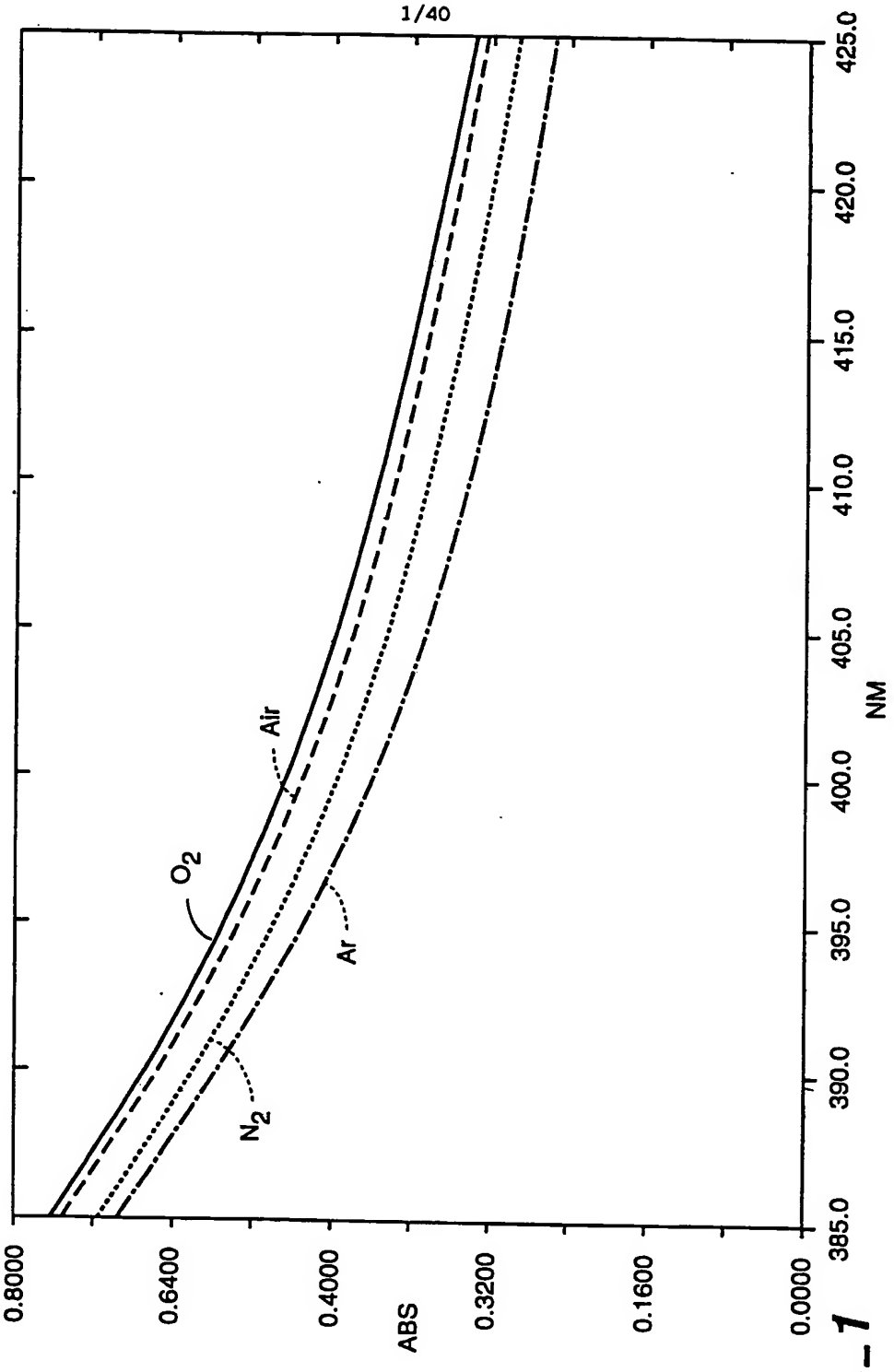
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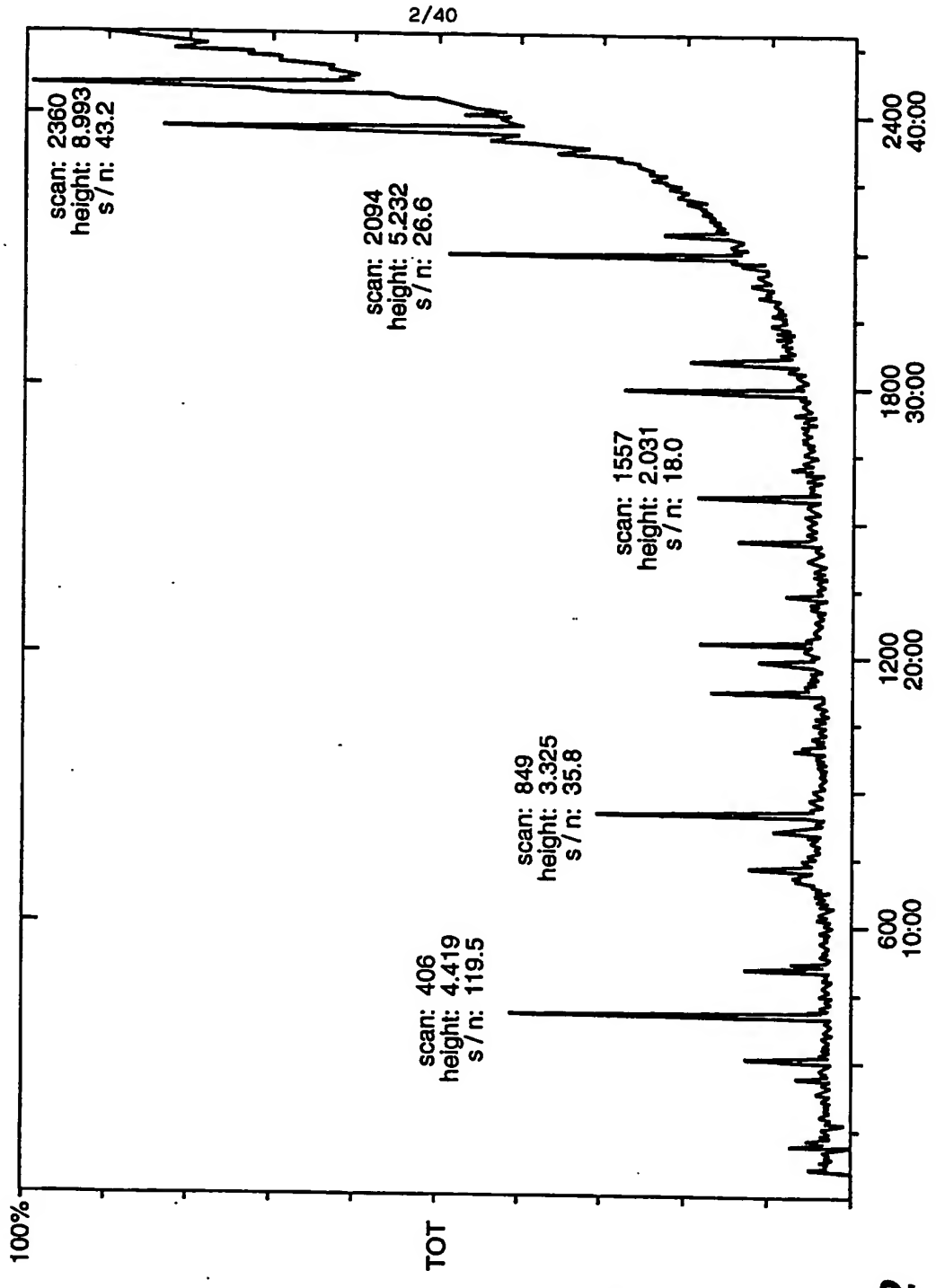
FIG._1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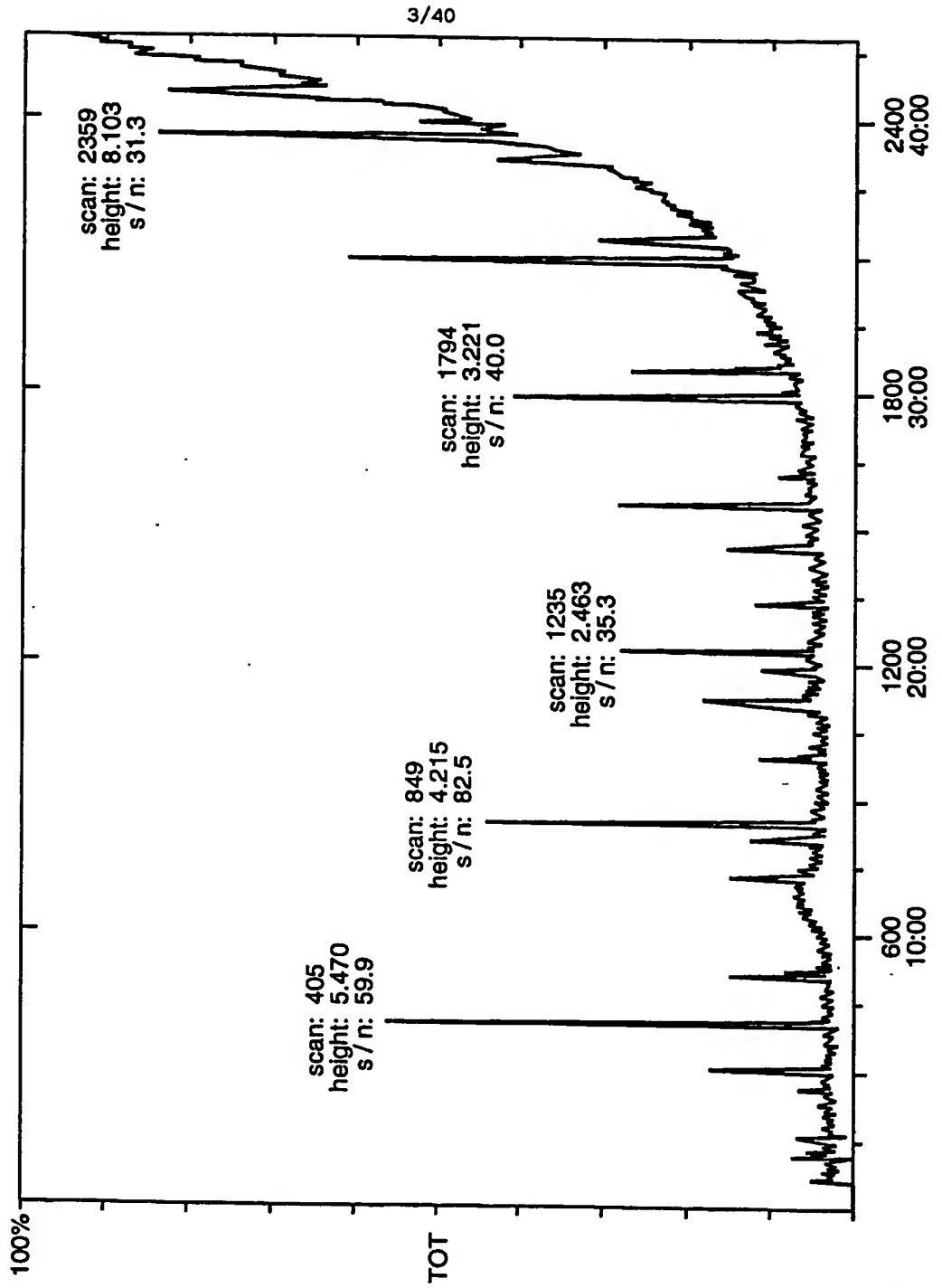
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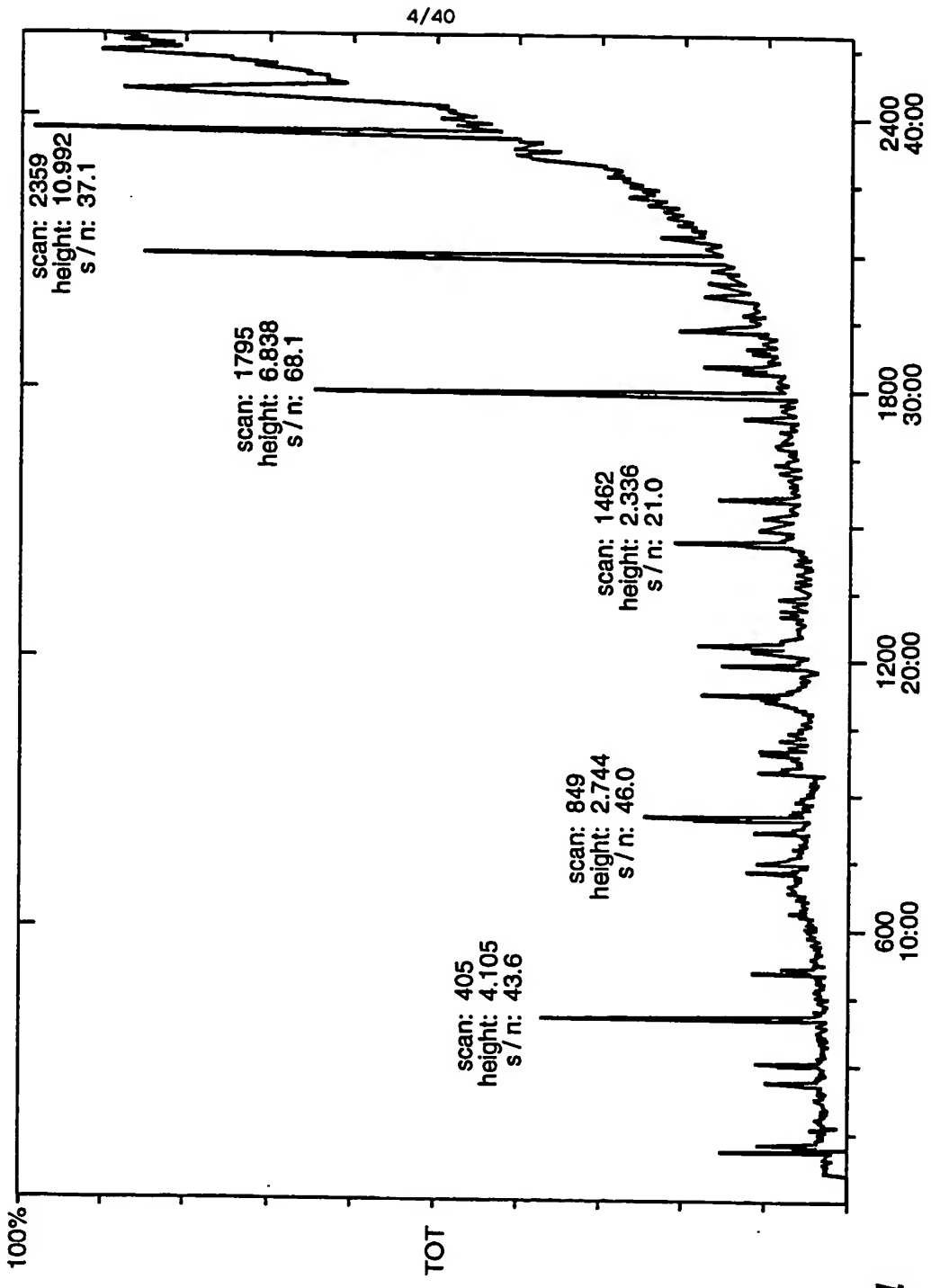
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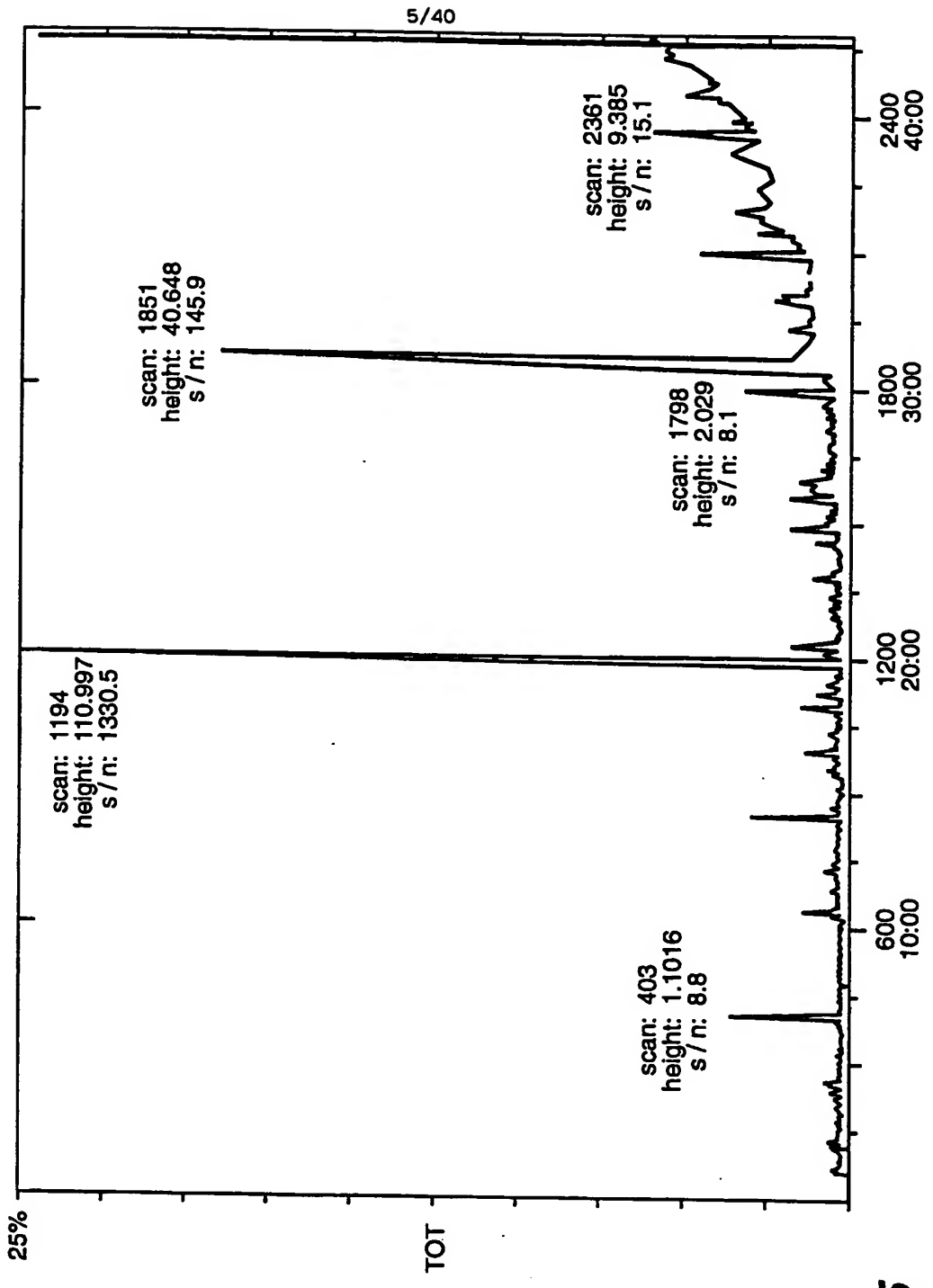
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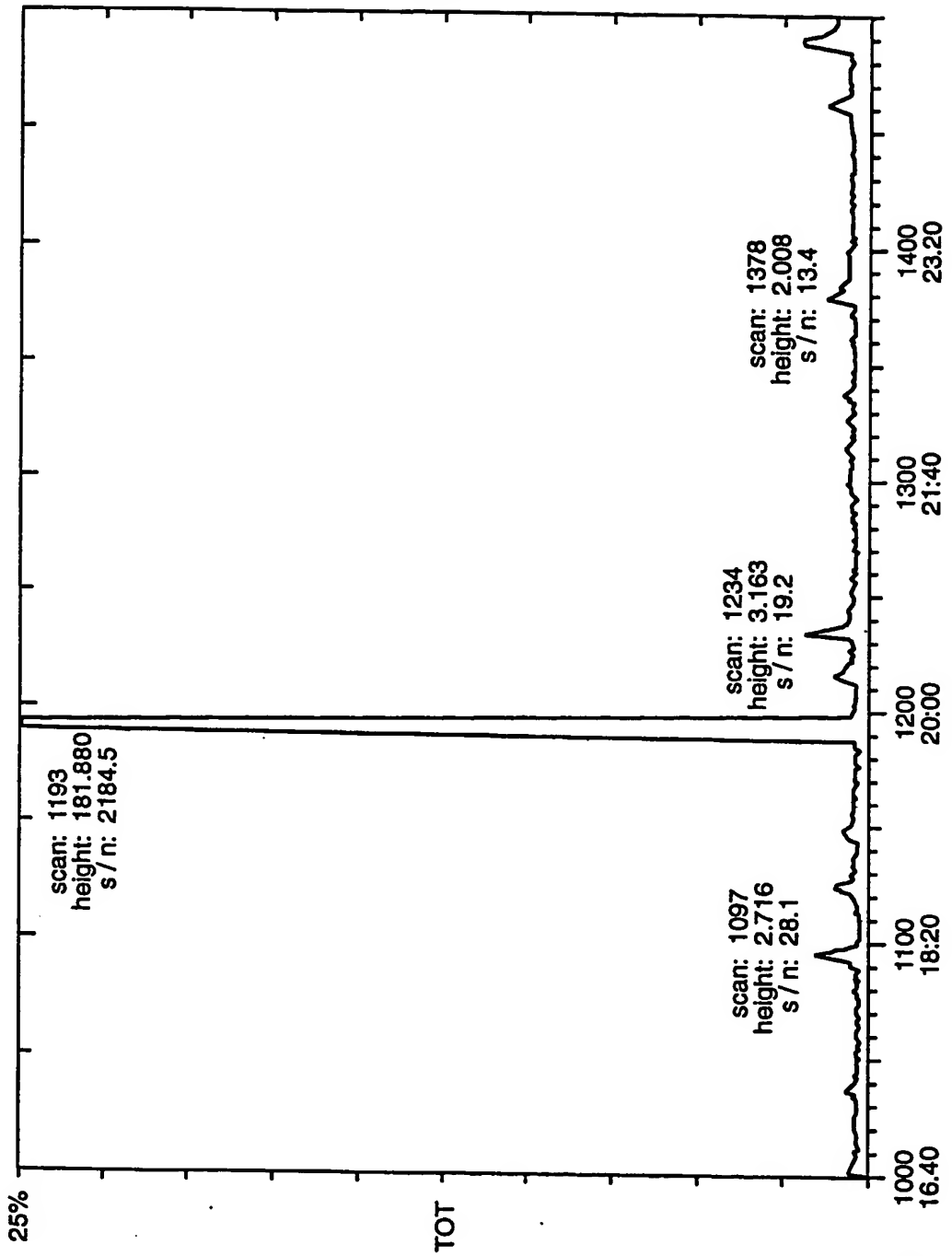
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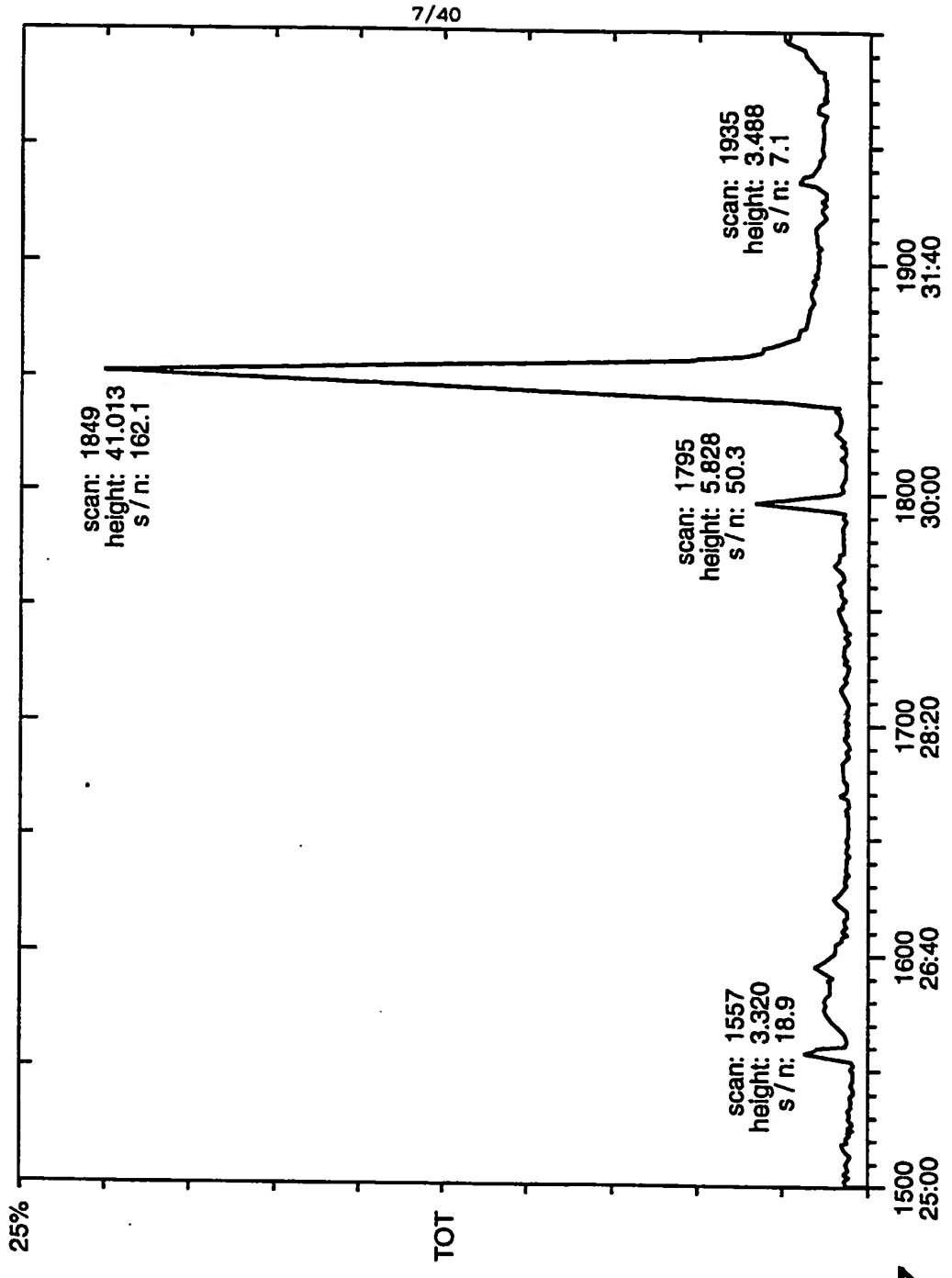
FIG._6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s/n: 18.9
scan: 1849
height: 41.013
s/n: 162.1
scan: 1795
height: 5.828
s/n: 50.3
scan: 1935
height: 3.488
s/n: 7.1
1500
25:00
1600
26:40
1700
28:20
1800
30:00
1900
31:40

FIG._7

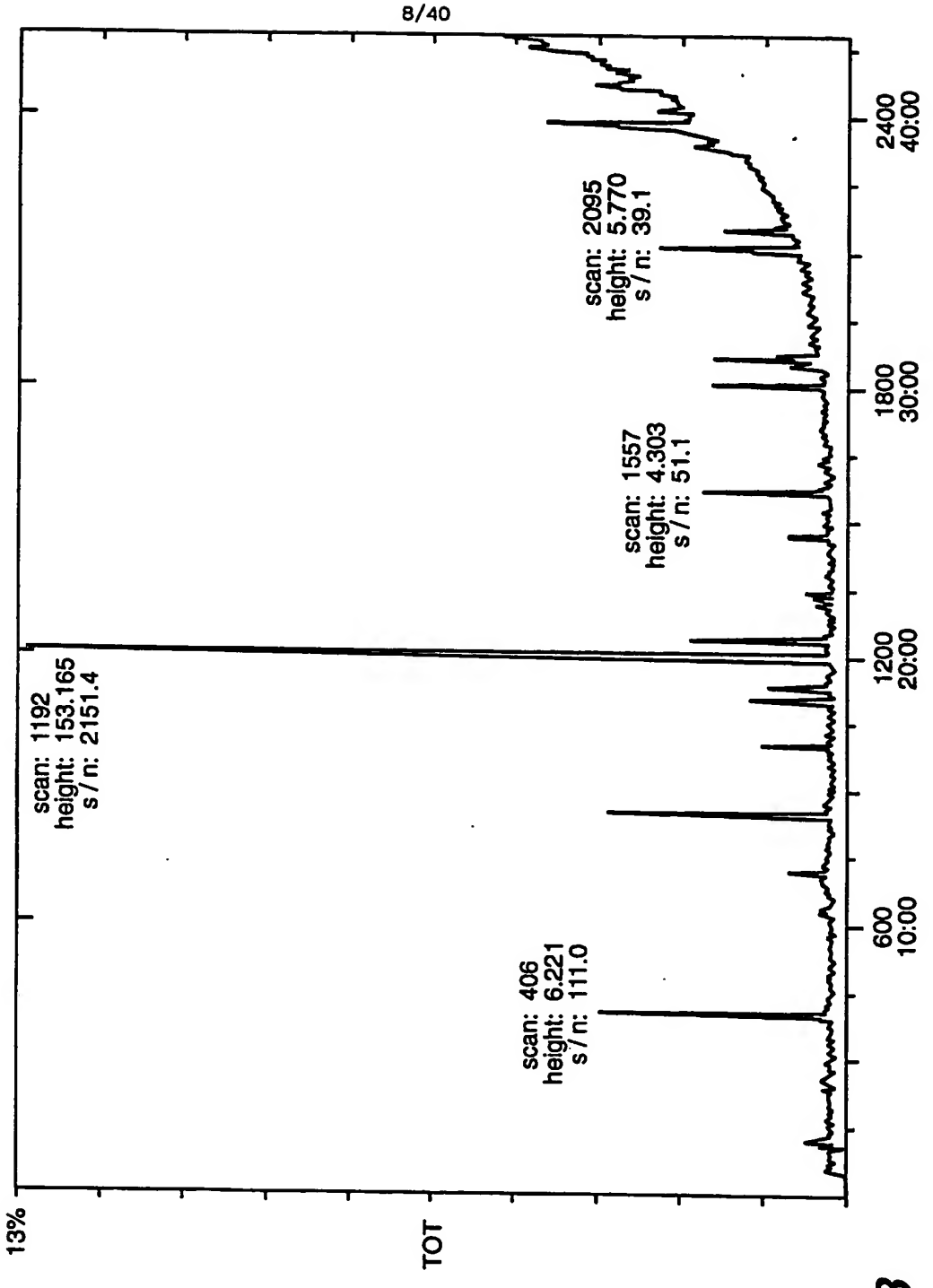
scan: 1192
height: 153.165
s/n: 2151.4
scan: 406
height: 6.221
s/n: 111.0
scan: 1557
height: 4.303
s/n: 51.1
scan: 2095
height: 5.770
s/n: 39.1
13%
TOT
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._8

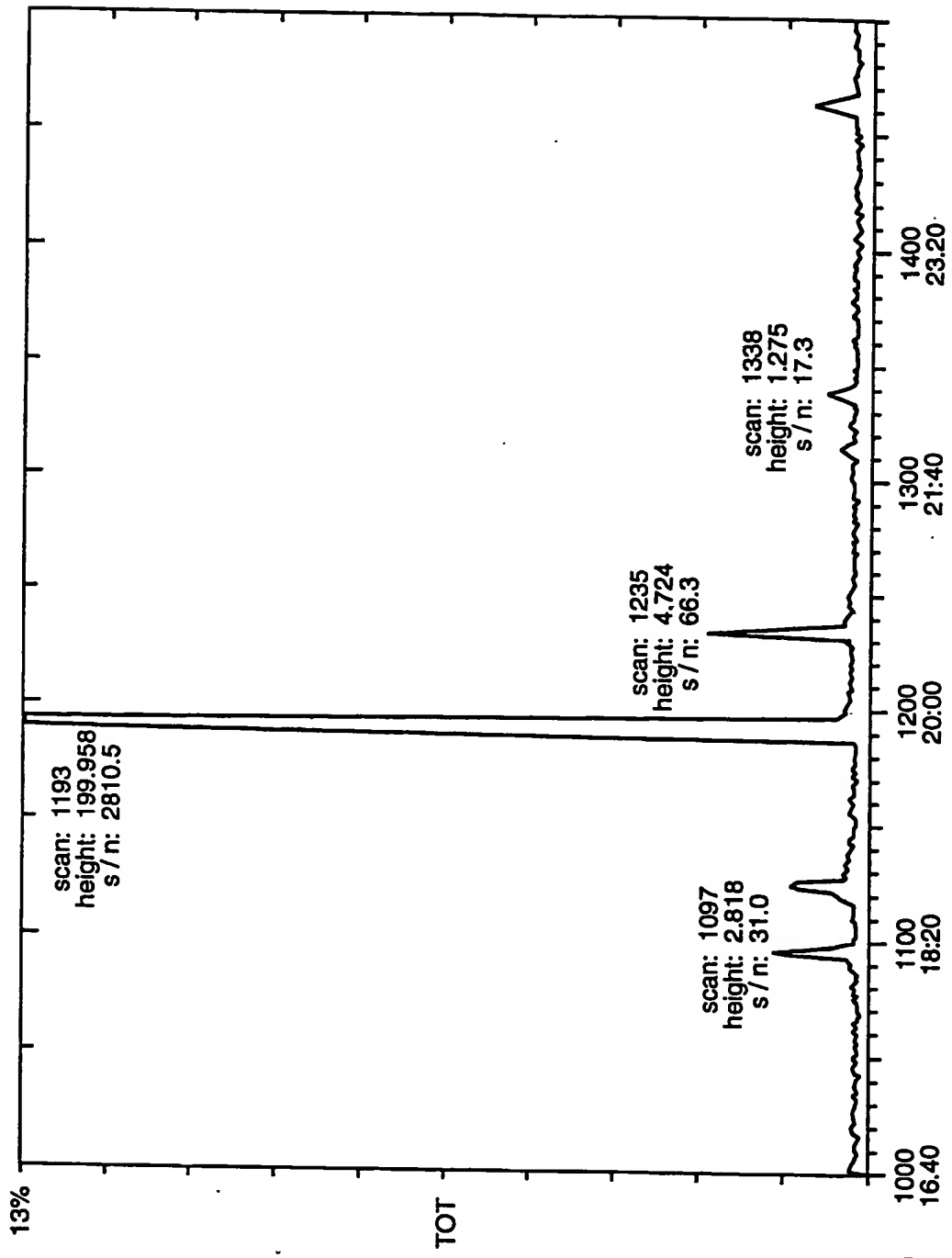
13%
TOT
scan: 1193
height: 199.958
s/n: 2810.5
scan: 1097
height: 2.818
s/n: 31.0
scan: 1235
height: 4.724
s/n: 66.3
scan: 1338
height: 1.275
s/n: 17.3
1000
16.40
1100
18:20
1200
20:00
1300
21:40
1400
23.20

FIG._9

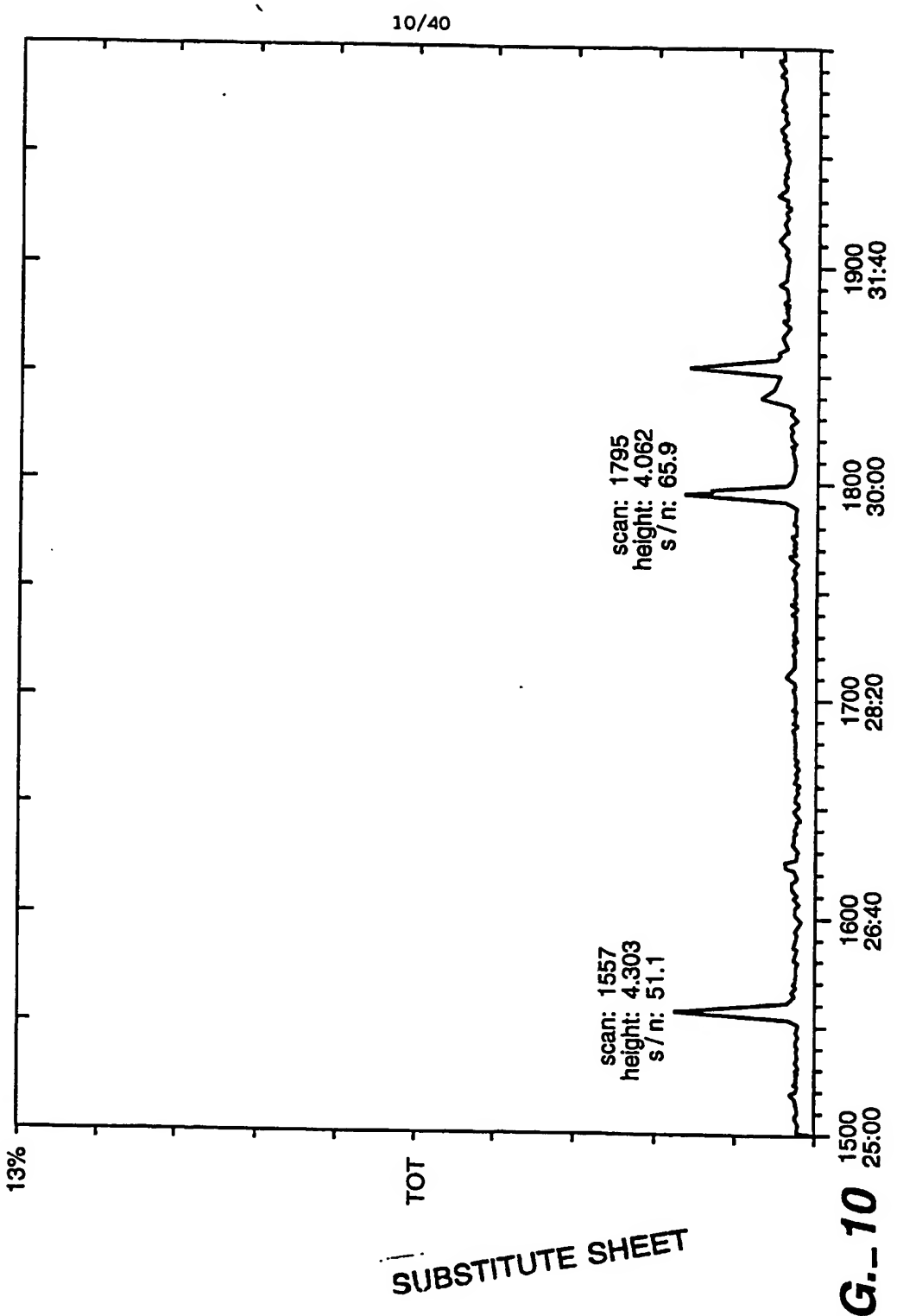

FIG._10

SUBSTITUTE SHEET

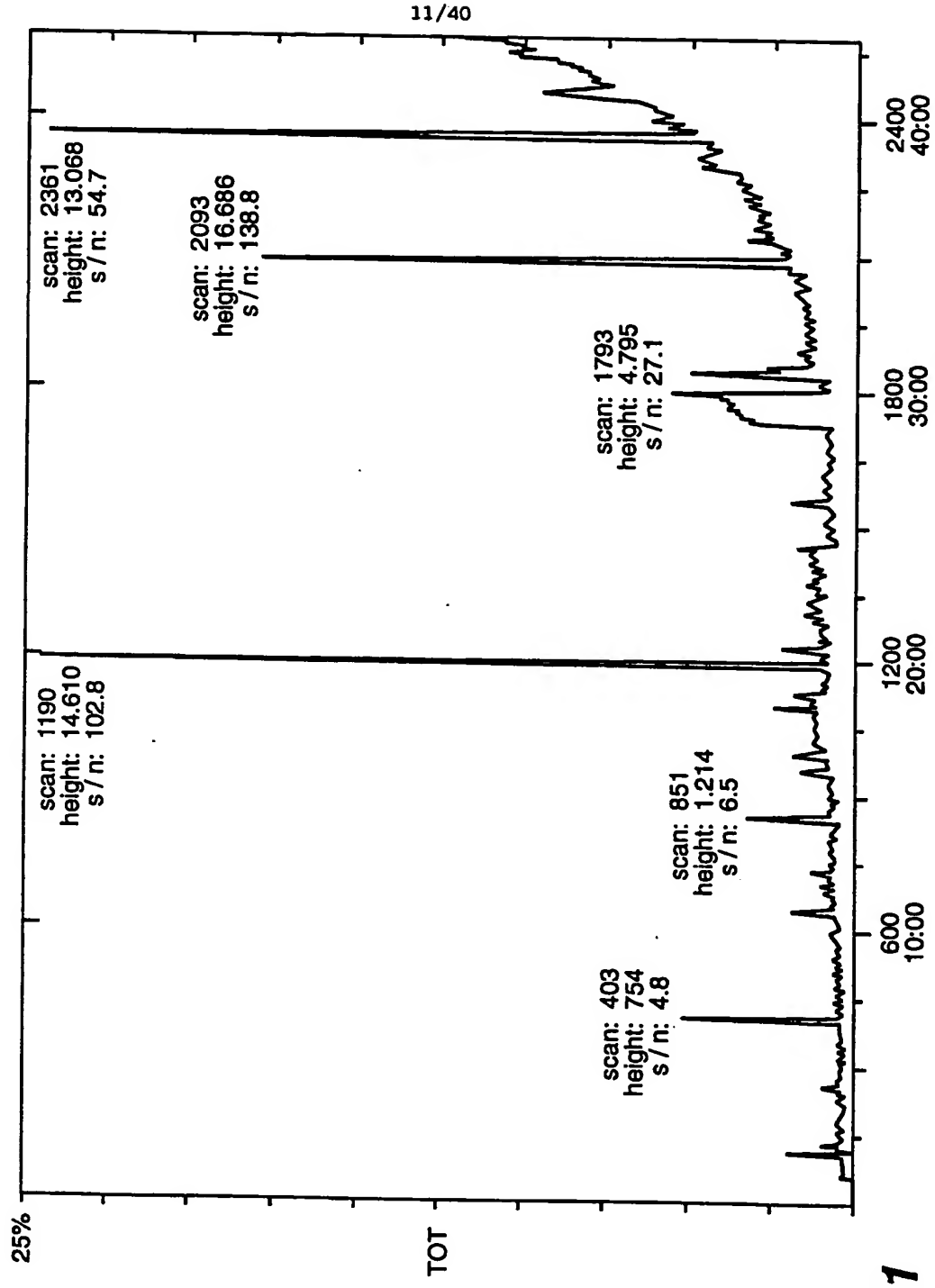
scan: 2361
height: 13.068
s/n: 54.7
scan: 2093
height: 16.686
s/n: 138.8
scan: 1793
height: 4.795
s/n: 27.1
scan: 1190
height: 14.610
s/n: 102.8
scan: 851
height: 1.214
s/n: 6.5
scan: 403
height: 754
s/n: 4.8
25%
TOT
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._11

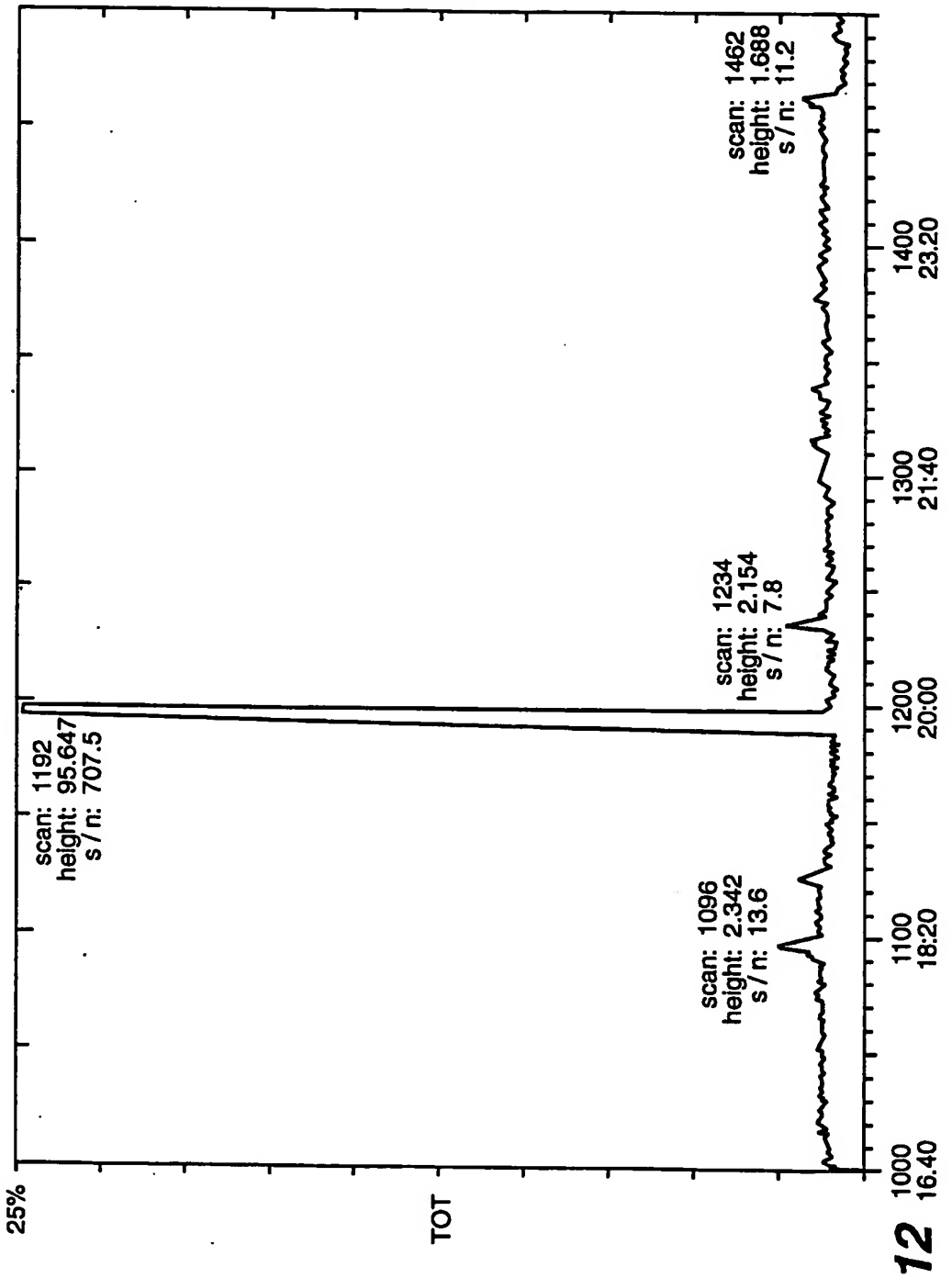
25%
TOT
scan: 1192
height: 95.647
s/n: 707.5
scan: 1096
height: 2.342
s/n: 13.6
scan: 1234
height: 2.154
s/n: 7.8
scan: 1462
height: 1.688
s/n: 11.2
1000
16.40
1100
18:20
1200
20:00
1300
21:40
1400
23.20

FIG._12

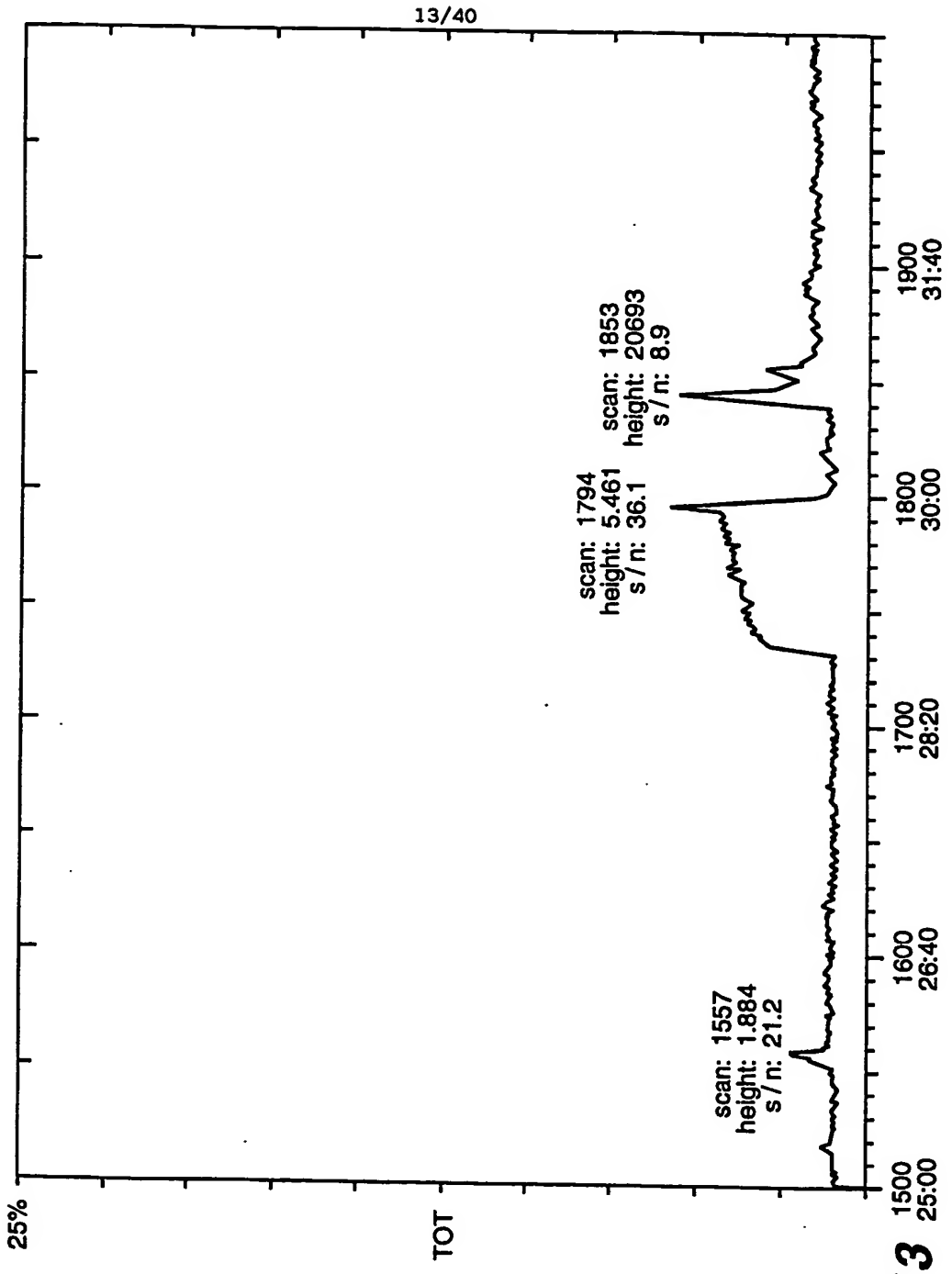
25%
TOT
1500
25:00
1600
26:40
1700
28:20
1800
30:00
1900
31:40
scan: 1557
height: 1.884
s/n: 21.2
scan: 1794
height: 5.461
s/n: 36.1
scan: 1853
height: 20693
s/n: 8.9

FIG._13

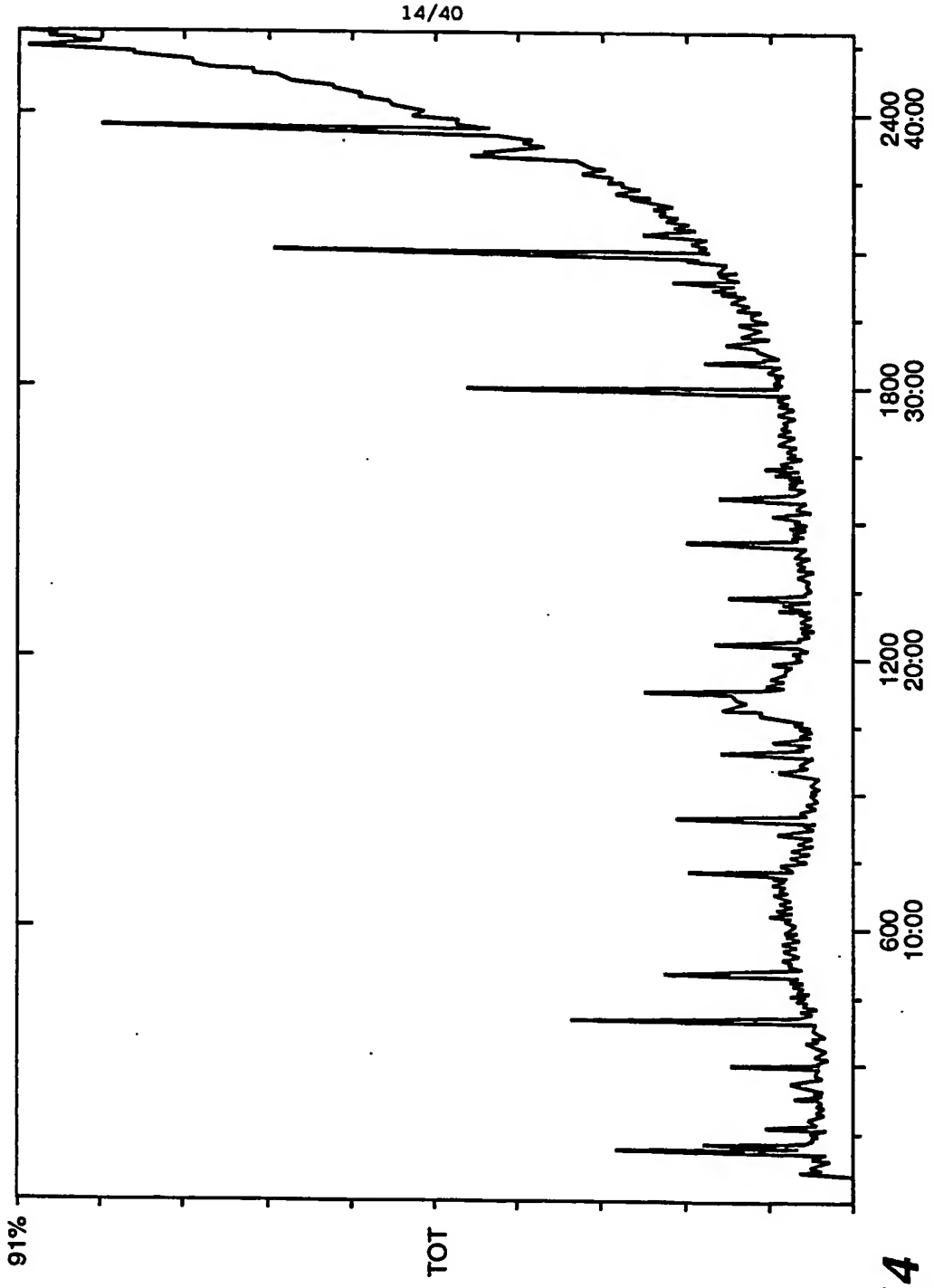

FIG._14

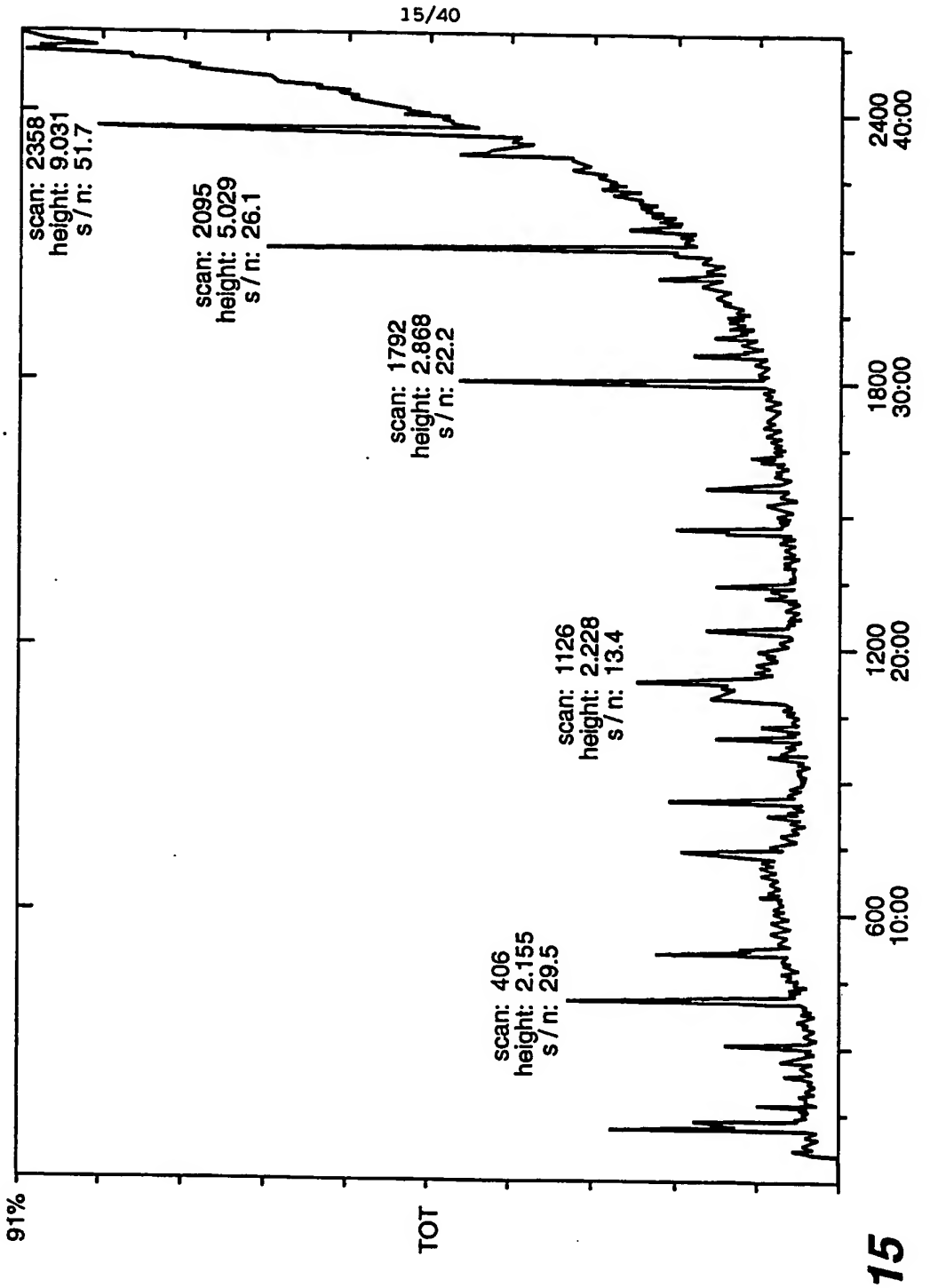
scan: 2358
height: 9.031
s/n: 51.7
scan: 2095
height: 5.029
s/n: 26.1
scan: 1792
height: 2.868
s/n: 22.2
scan: 1126
height: 2.228
s/n: 13.4
scan: 406
height: 2.155
s/n: 29.5
91%
TOT
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._15

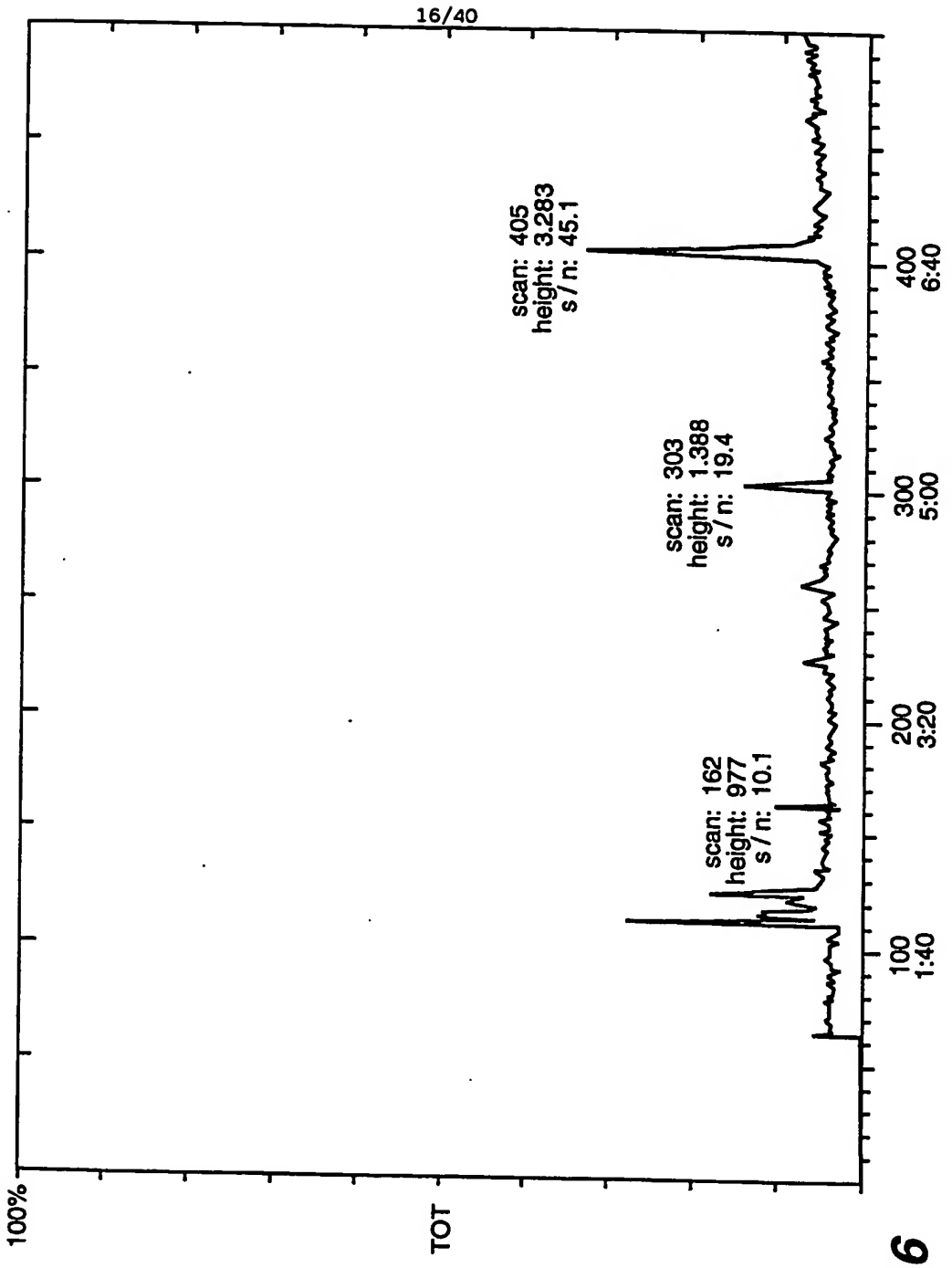
16/40
scan: 405
height: 3.283
s/n: 45.1
scan: 303
height: 1.388
s/n: 19.4
scan: 162
height: 977
s/n: 10.1
100%
TOT
100
1:40
200
3:20
300
5:00
400
6:40

FIG._16

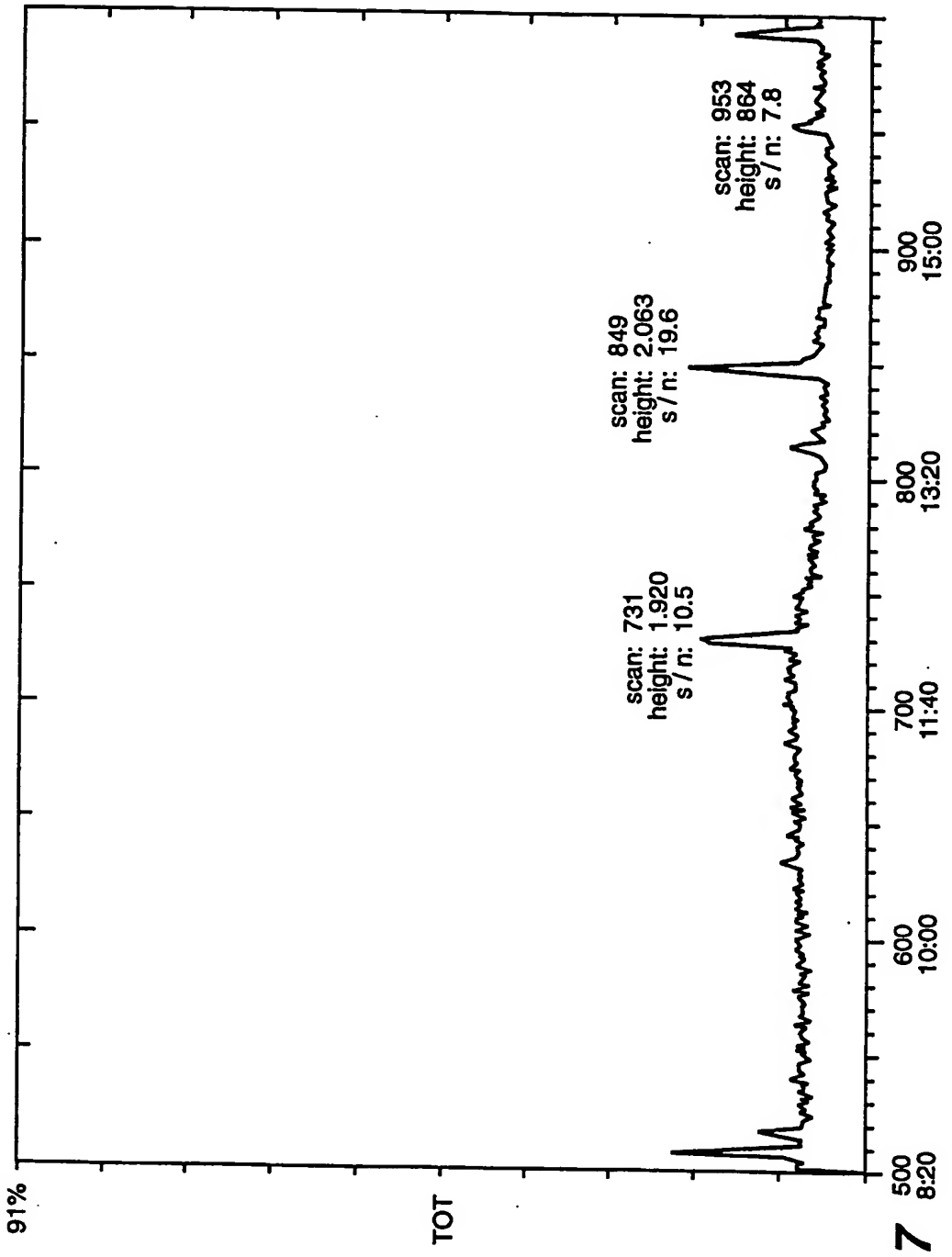
91%
TOT
scan: 731
height: 1.920
s/n: 10.5
scan: 849
height: 2.063
s/n: 19.6
scan: 953
height: 864
s/n: 7.8
500
8:20
600
10:00
700
11:40
800
13:20
900
15:00

FIG._17

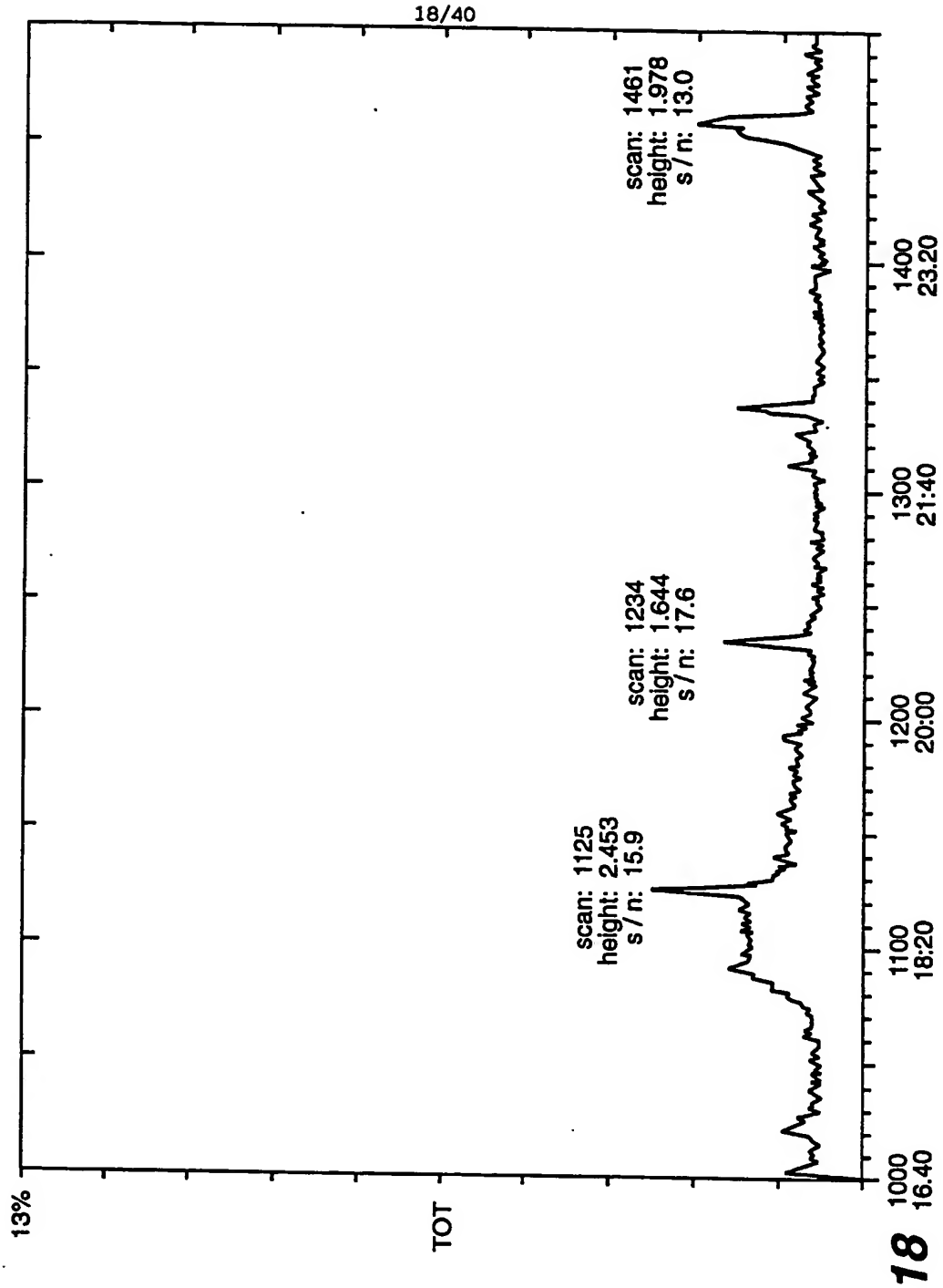
scan: 1461
height: 1.978
s/n: 13.0
scan: 1234
height: 1.644
s/n: 17.6
scan: 1125
height: 2.453
s/n: 15.9
13%
TOT
1000
16.40
1100
18:20
1200
20:00
1300
21:40
1400
23.20

FIG._18

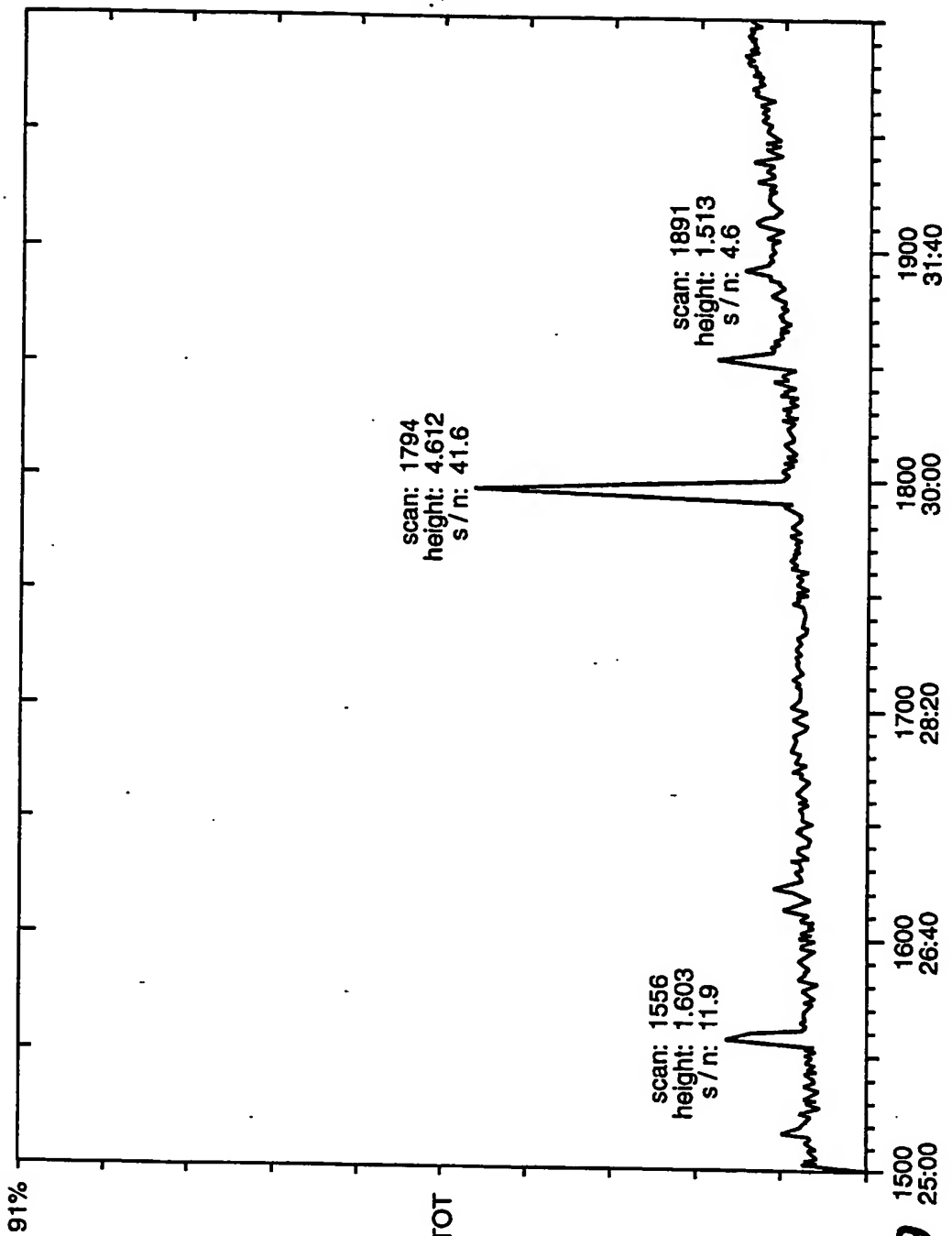
91%
TOT
scan: 1556
height: 1.603
s/n: 11.9
scan: 1794
height: 4.612
s/n: 41.6
scan: 1891
height: 1.513
s/n: 4.6
1500
25:00
1600
26:40
1700
28:20
1800
30:00
1900
31:40

FIG._19

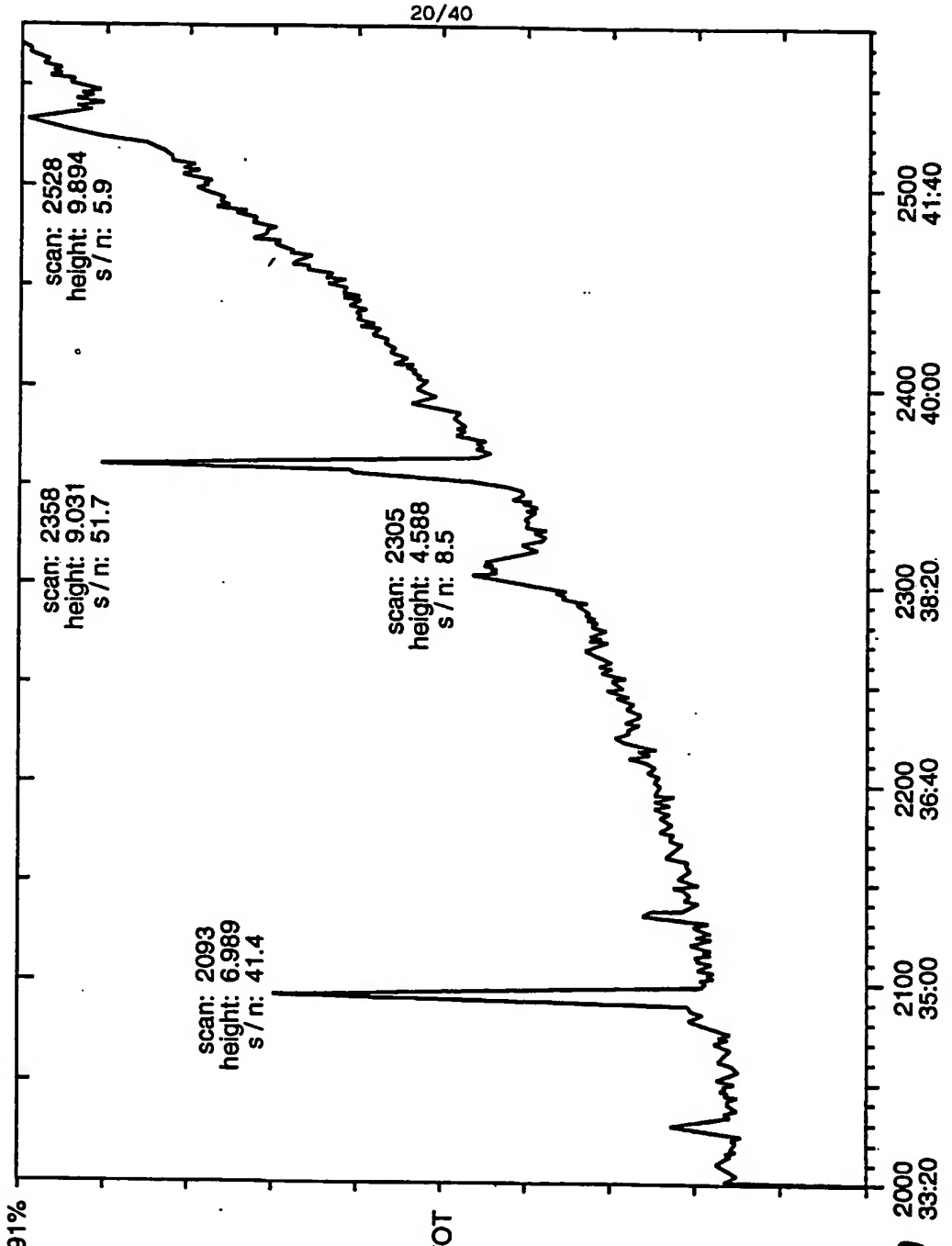
scan: 2528
height: 9.894
s/n: 5.9
scan: 2358
height: 9.031
s/n: 51.7
scan: 2305
height: 4.588
s/n: 8.5
scan: 2093
height: 6.989
s/n: 41.4
91%
TOT
2000
33:20
2100
35:00
2200
36:40
2300
38:20
2400
40:00
2500
41:40

FIG._20

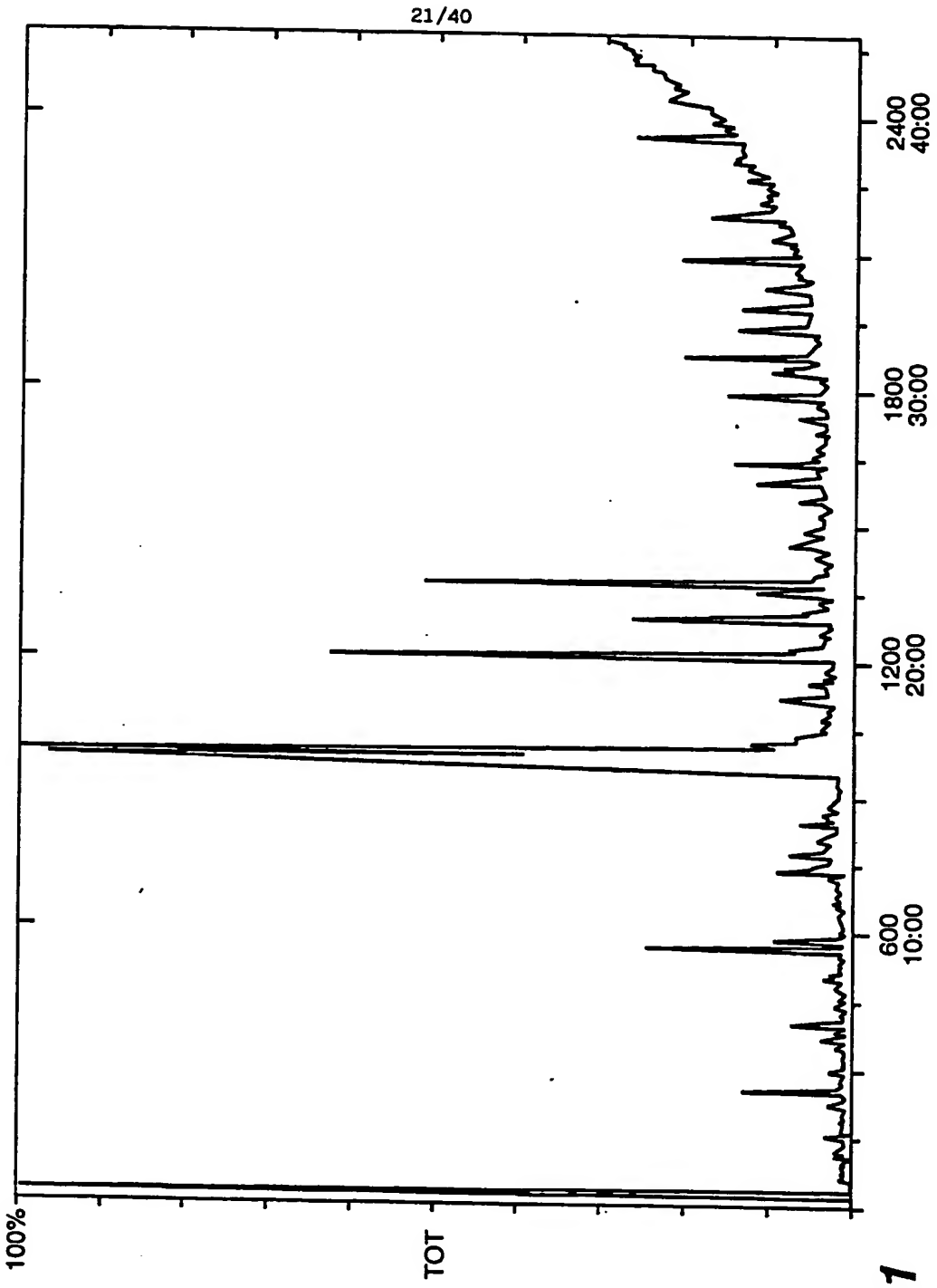

FIG._21

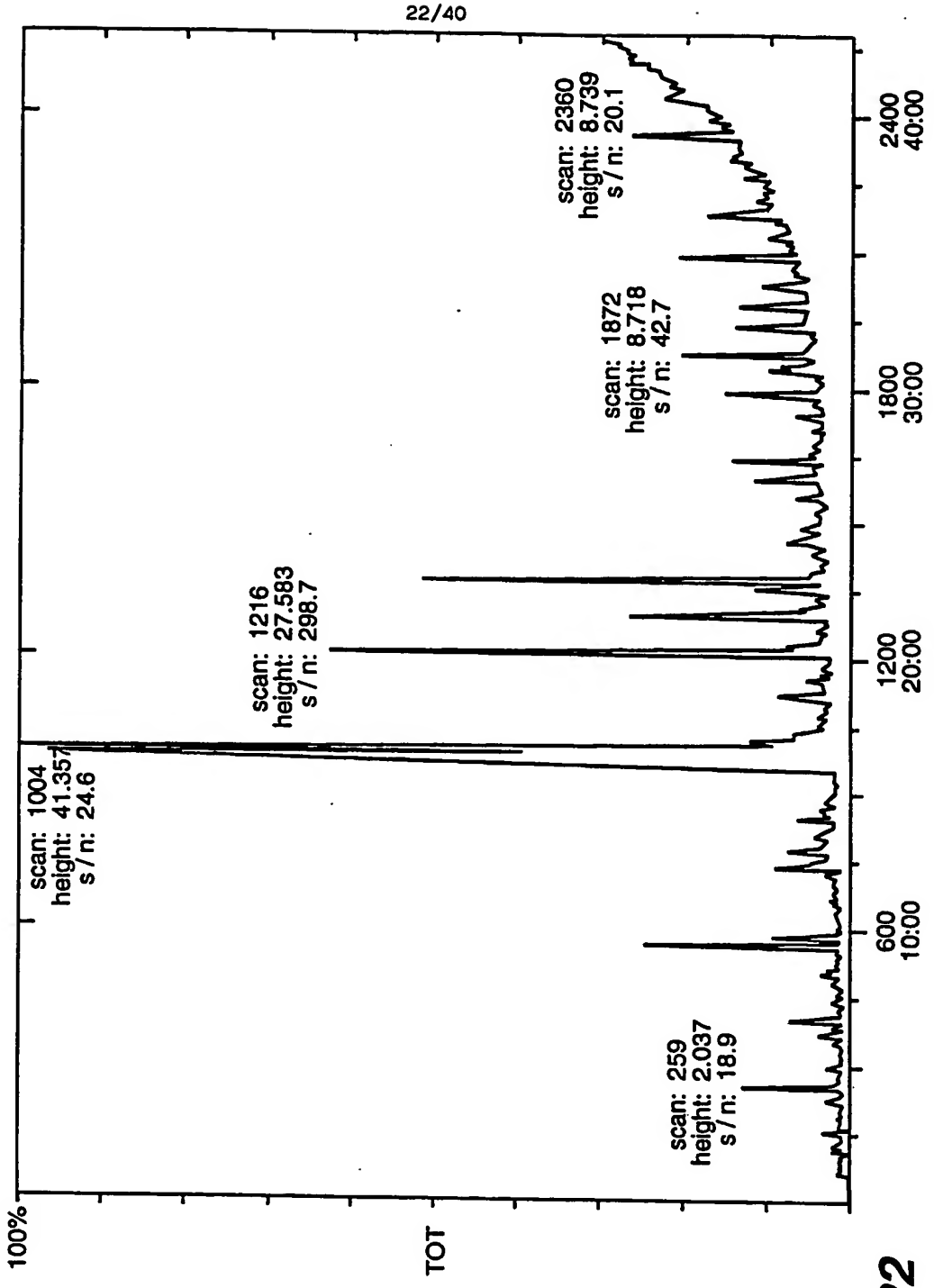
100%
TOT
scan: 1004
height: 41.357
s/n: 24.6
scan: 1216
height: 27.583
s/n: 298.7
scan: 259
height: 2.037
s/n: 18.9
scan: 1872
height: 8.718
s/n: 42.7
scan: 2360
height: 8.739
s/n: 20.1
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._22

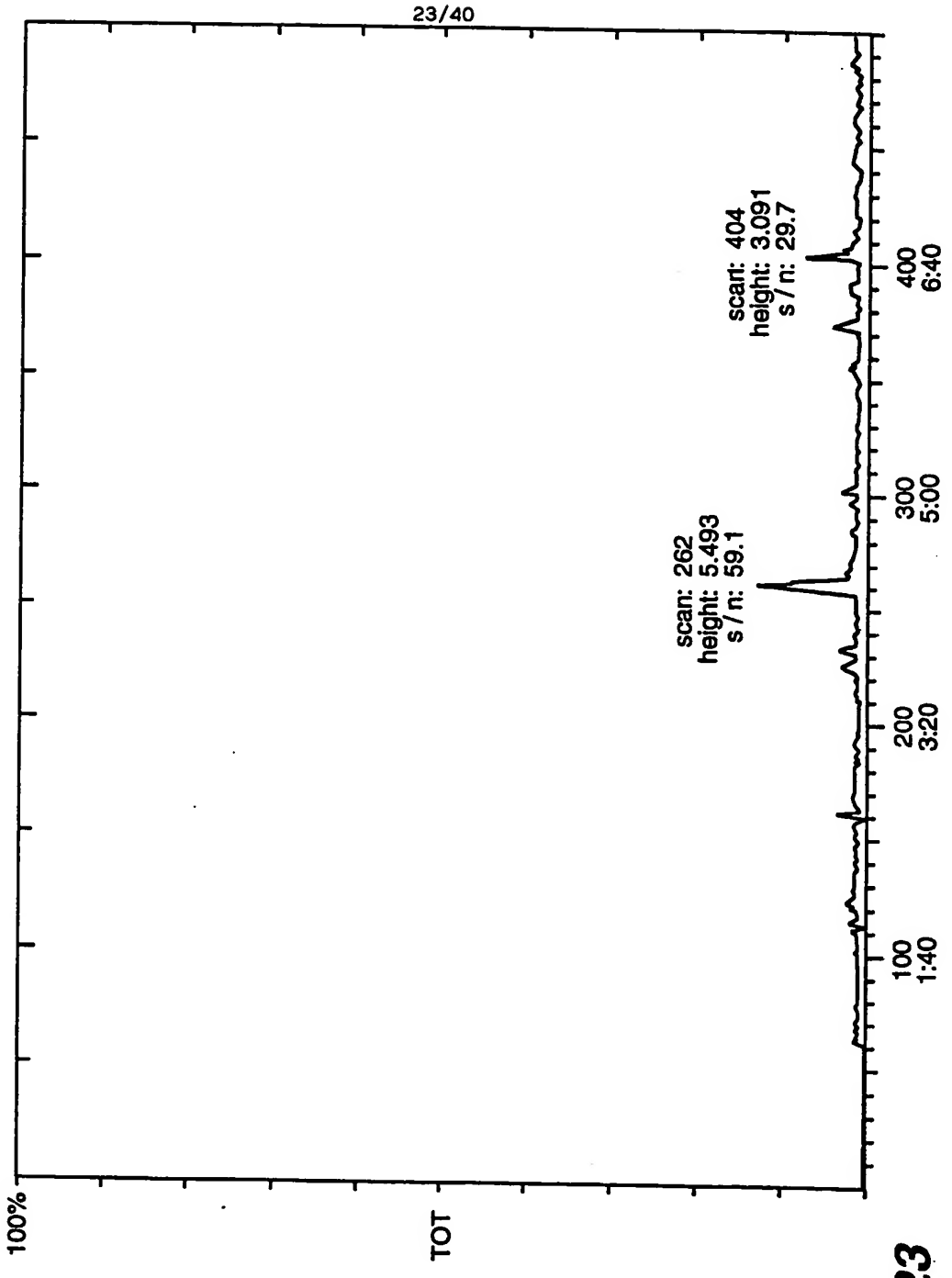
100%
TOT
scan: 262
height: 5.493
s/n: 59.1
scan: 404
height: 3.091
s/n: 29.7
100
1:40
200
3:20
300
5:00
400
6:40

FIG._23

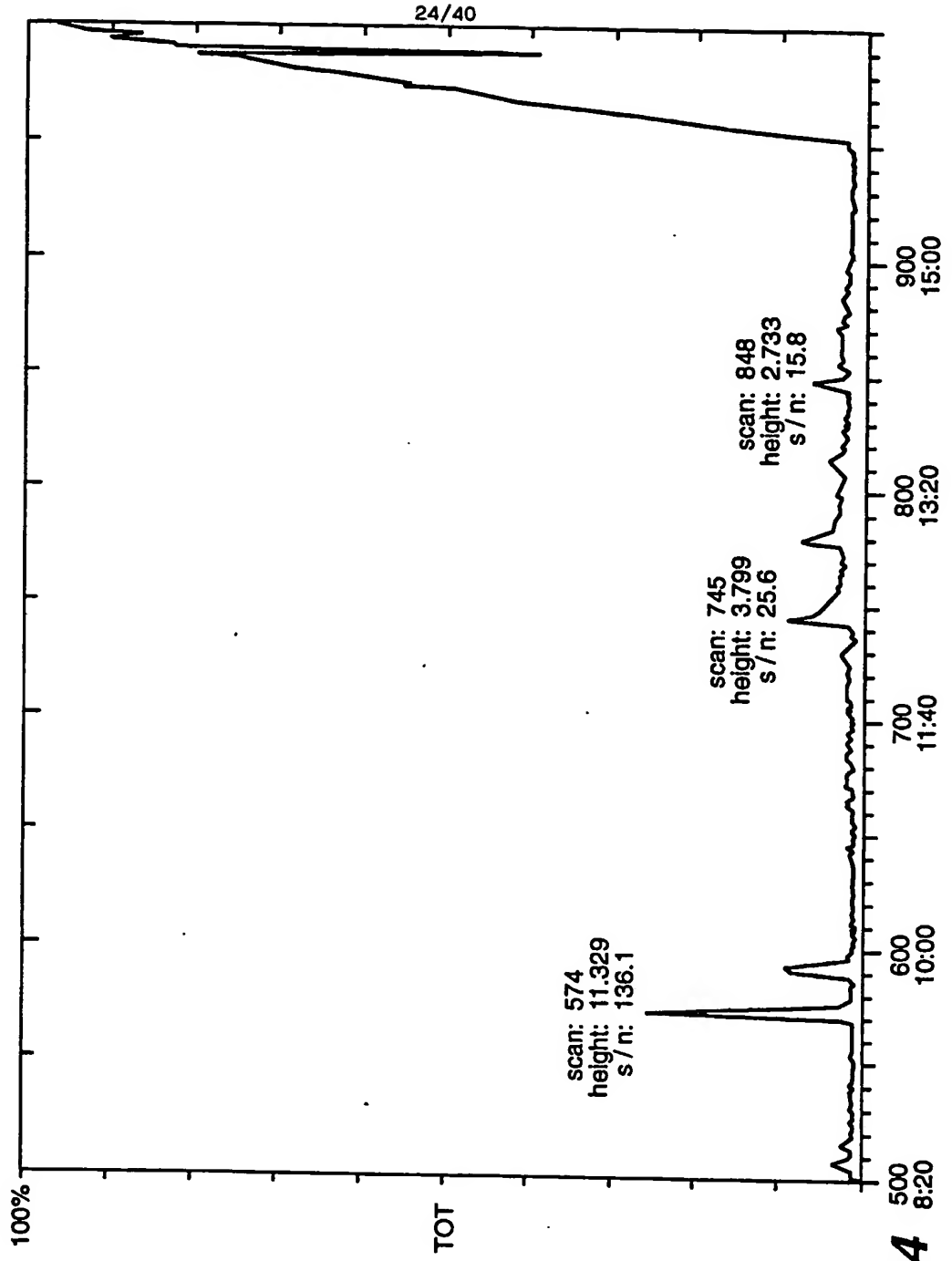
100%
TOT
scan: 574
height: 11.329
s/n: 136.1
scan: 745
height: 3.799
s/n: 25.6
scan: 848
height: 2.733
s/n: 15.8
500
8:20
600
10:00
700
11:40
800
13:20
900
15:00

FIG._24

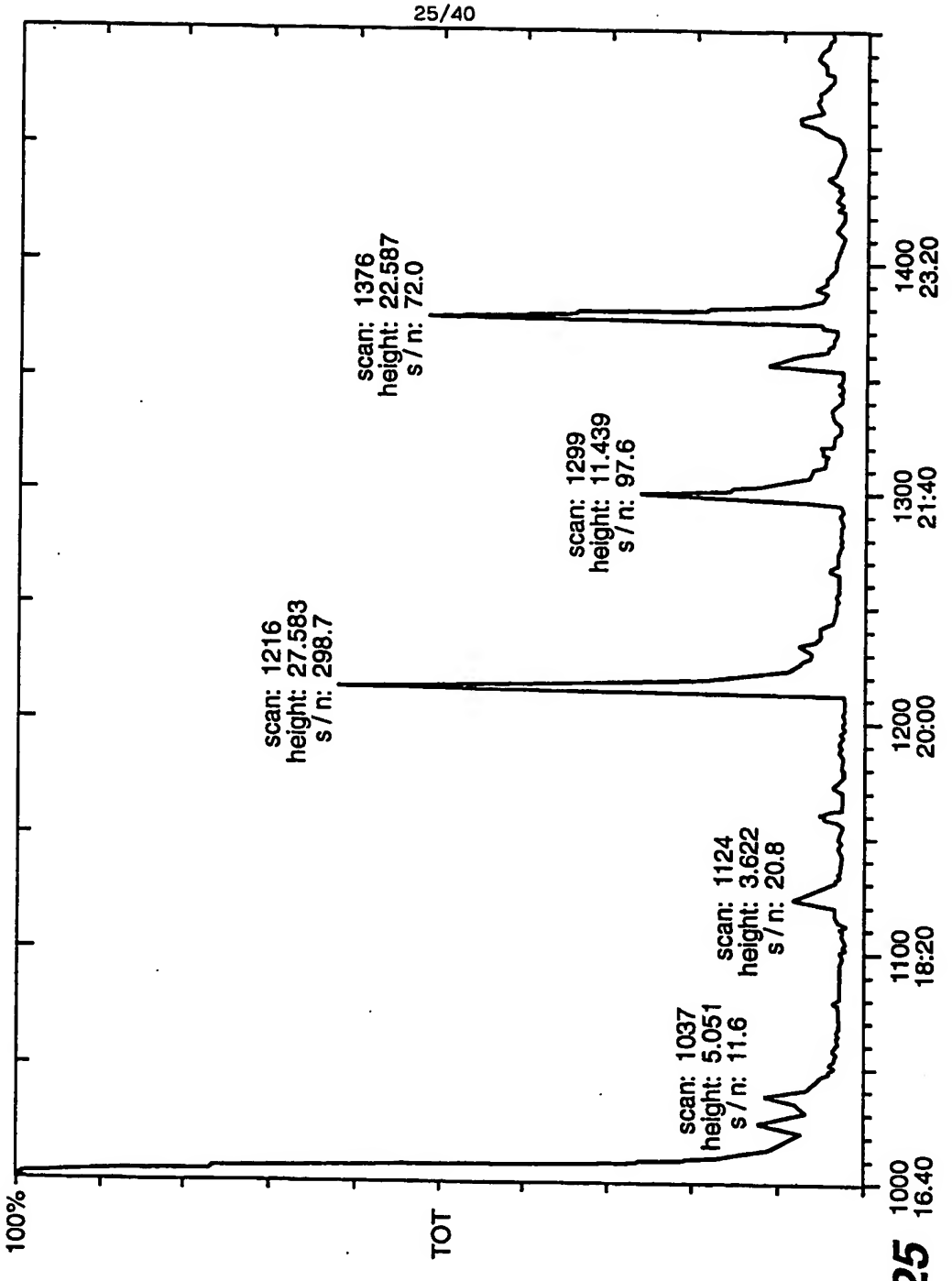
100%
TOT
scan: 1037
height: 5.051
s/n: 11.6
scan: 1124
height: 3.622
s/n: 20.8
scan: 1216
height: 27.583
s/n: 298.7
scan: 1299
height: 11.439
s/n: 97.6
scan: 1376
height: 22.587
s/n: 72.0
1000
16.40
1100
18:20
1200
20:00
1300
21:40
1400
23.20

FIG._25

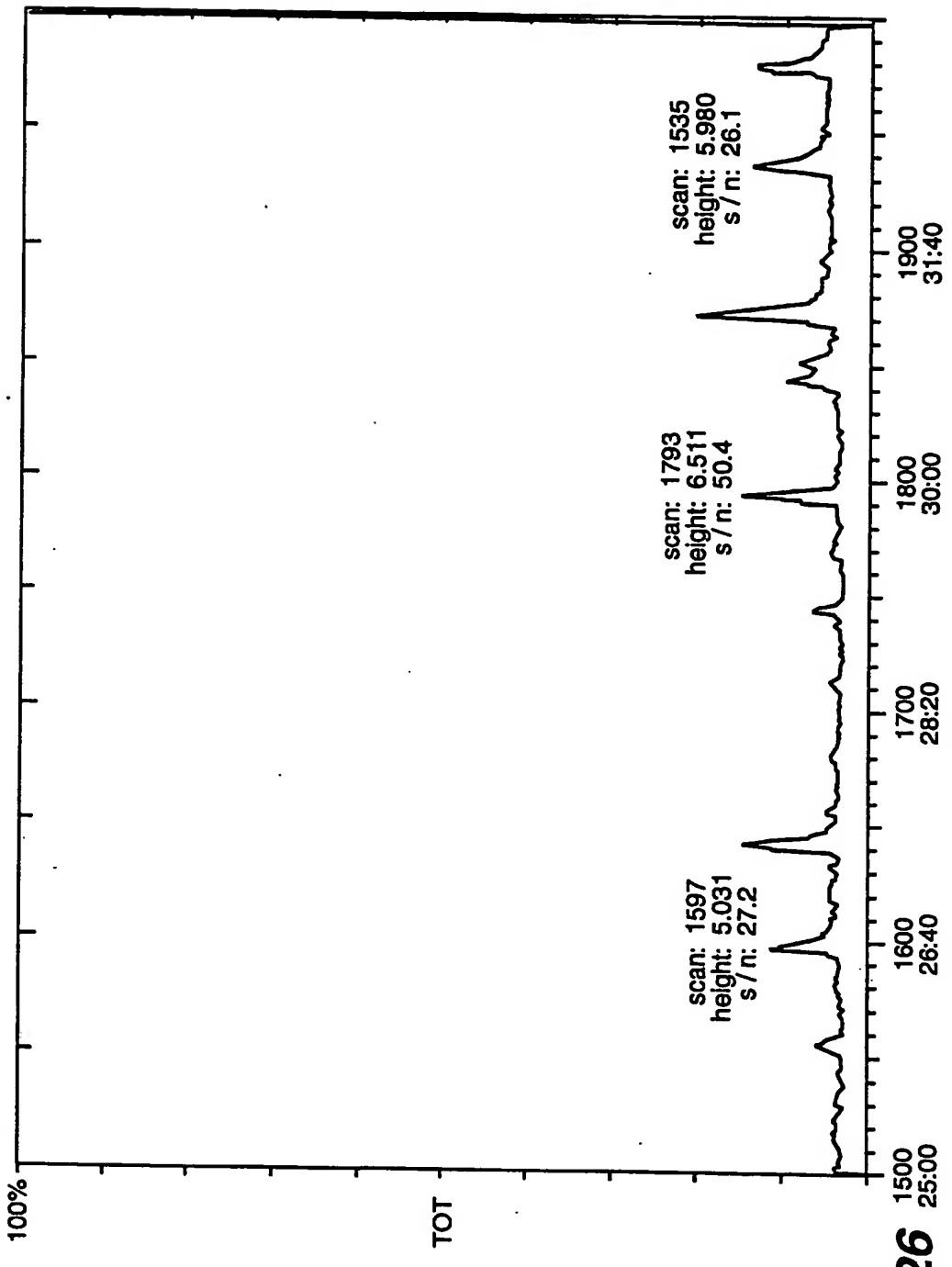

FIG._26

SUBSTITUTE SHEET

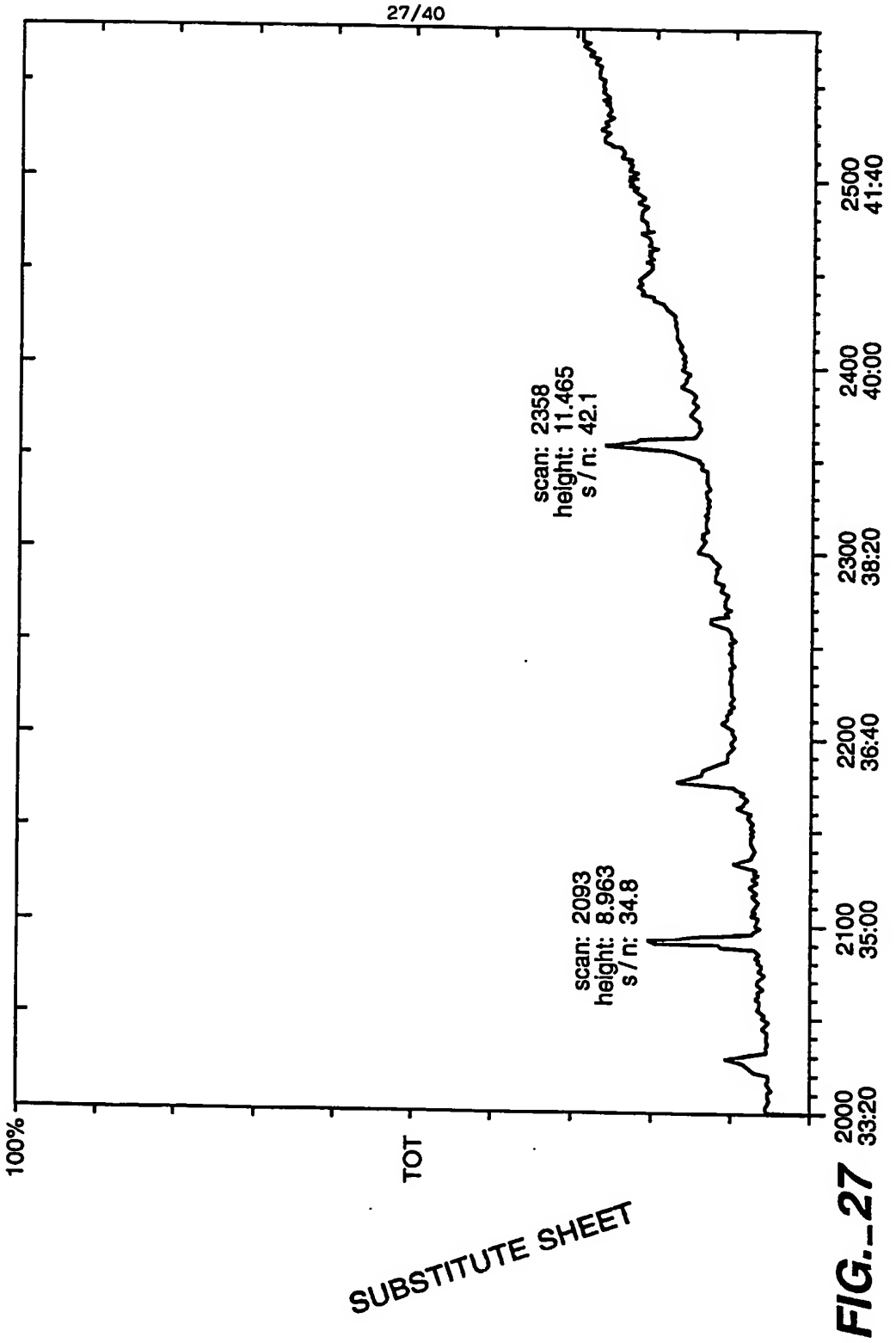
100%
TOT
scan: 2093
height: 8.963
s/n: 34.8
scan: 2358
height: 11.465
s/n: 42.1
2000
33:20
2100
35:00
2200
36:40
2300
38:20
2400
40:00
2500
41:40

FIG._27

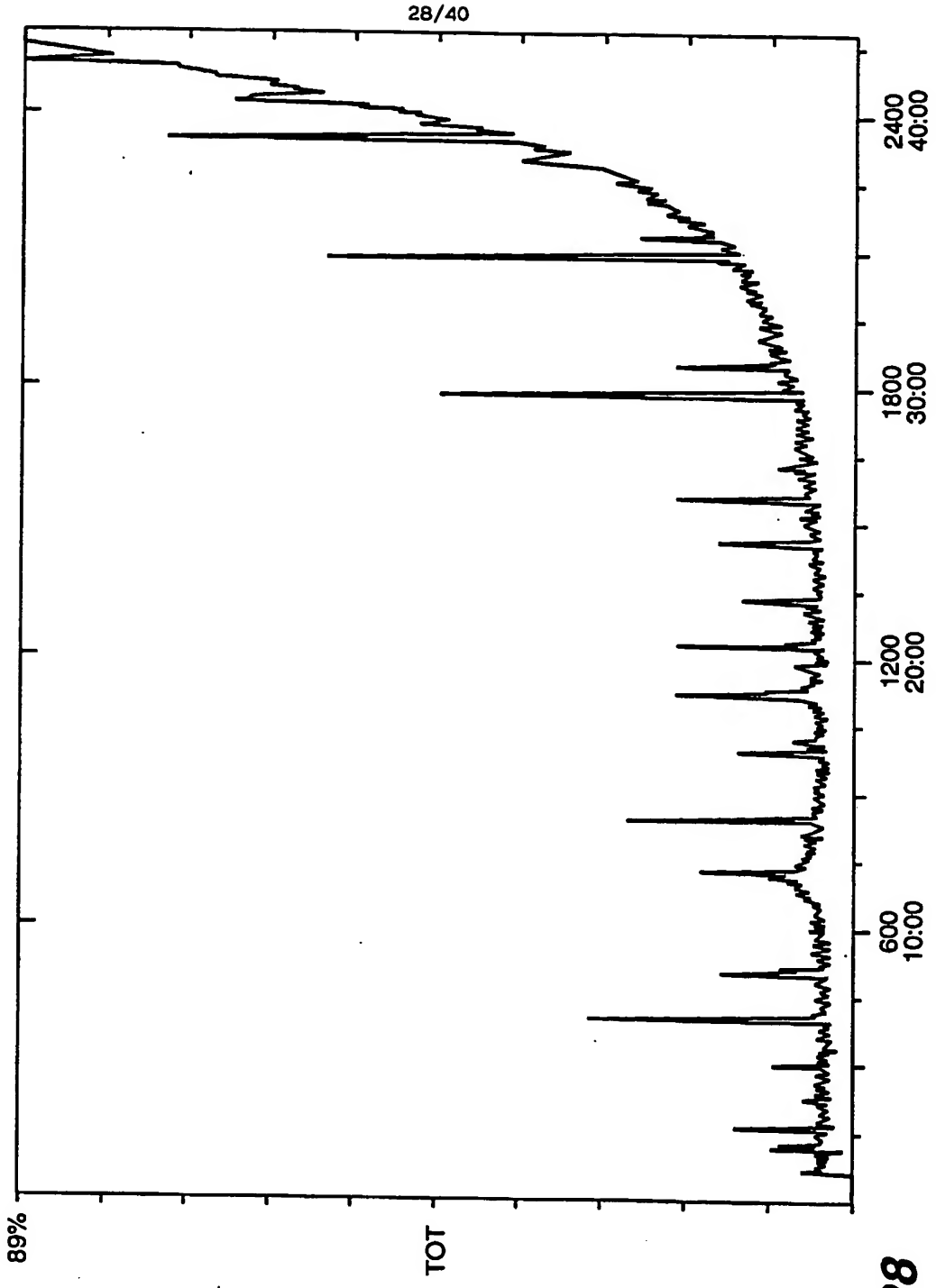

FIG._28

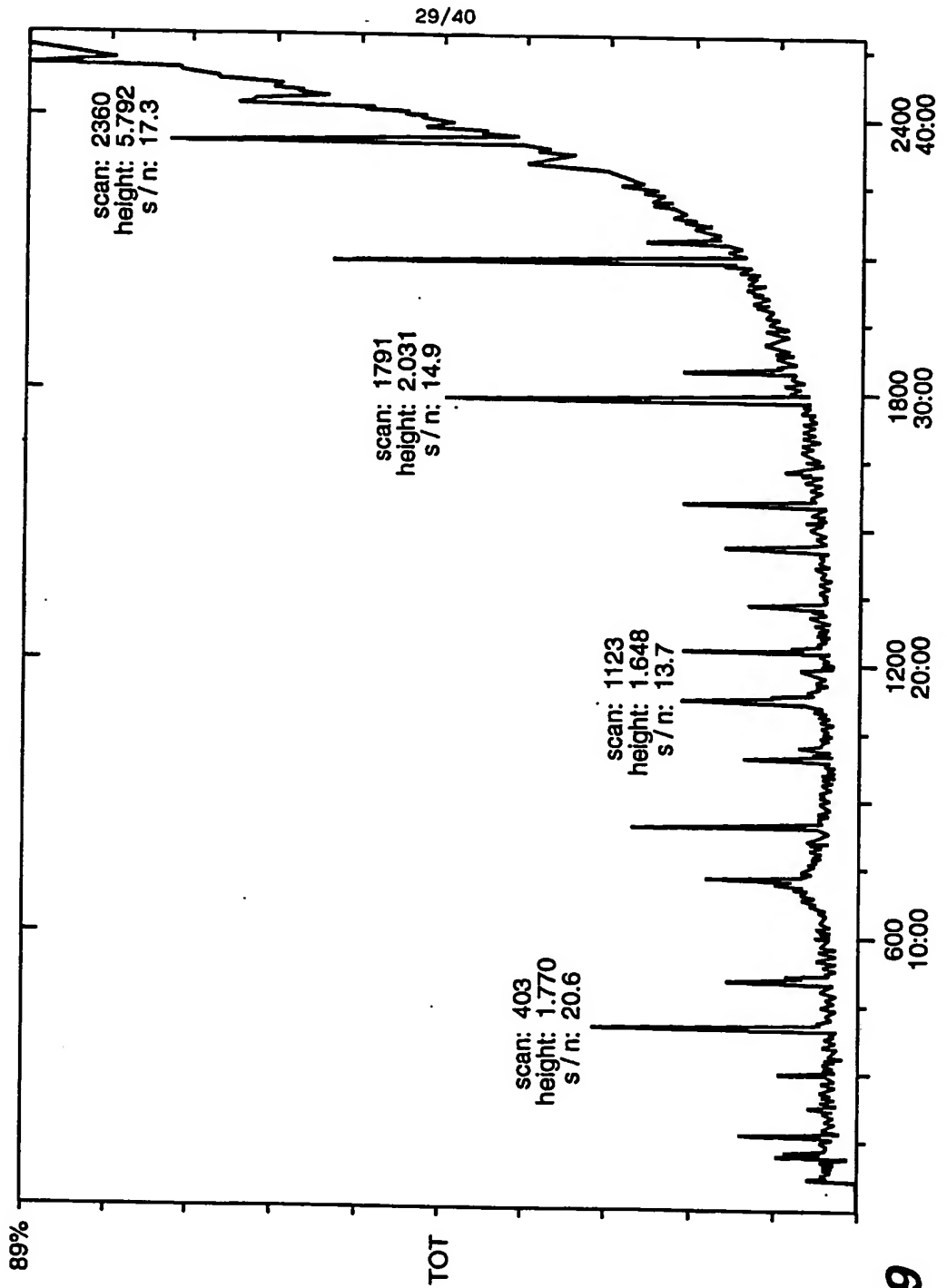
scan: 2360
height: 5.792
s/n: 17.3
scan: 1791
height: 2.031
s/n: 14.9
scan: 1123
height: 1.648
s/n: 13.7
scan: 403
height: 1.770
s/n: 20.6
89%
TOT
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._29

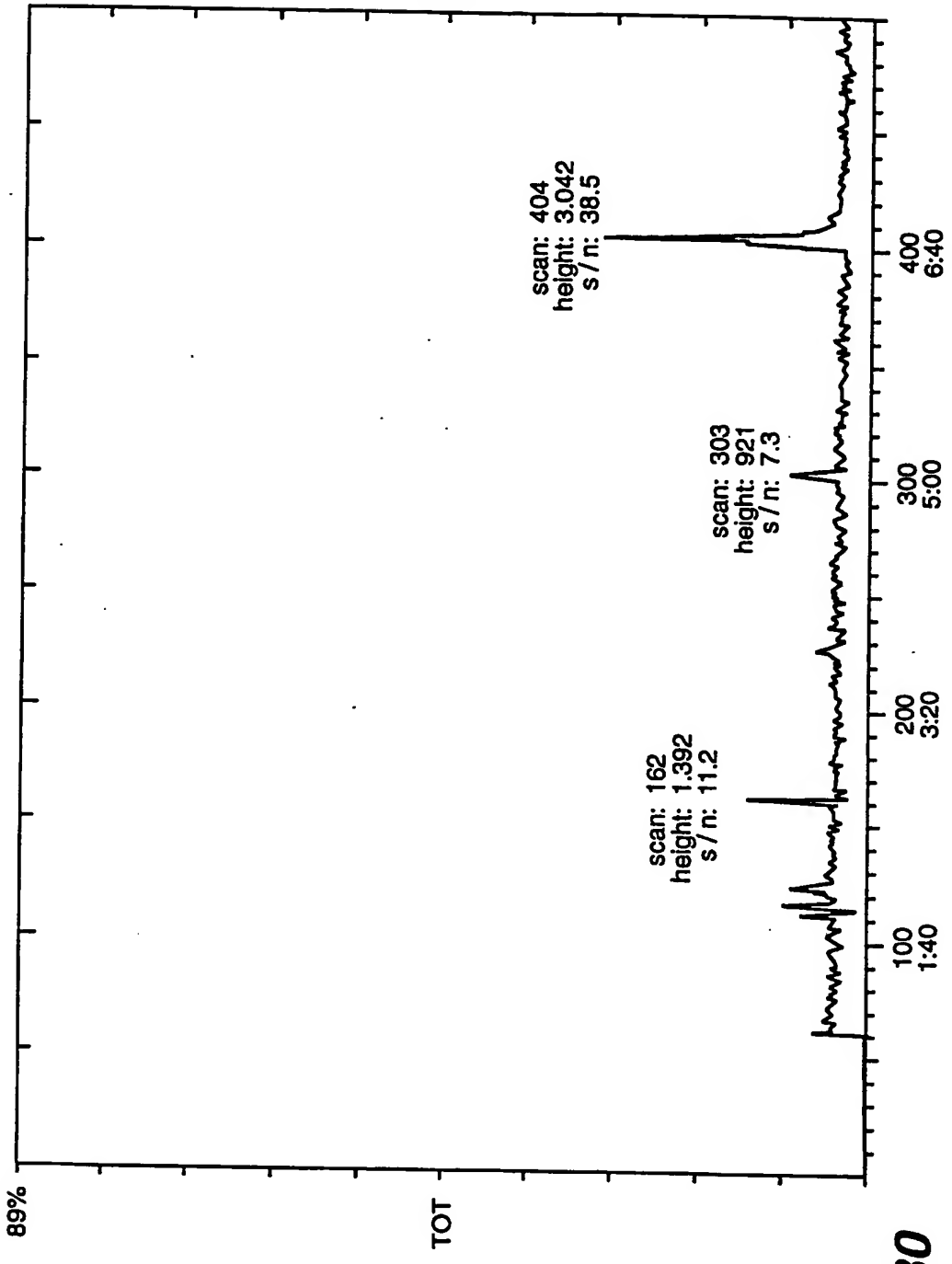
scan: 404
height: 3.042
s/n: 38.5
scan: 303
height: 921
s/n: 7.3
scan: 162
height: 1.392
s/n: 11.2
400
6:40
300
5:00
200
3:20
100
1:40
89%
TOT

FIG._30

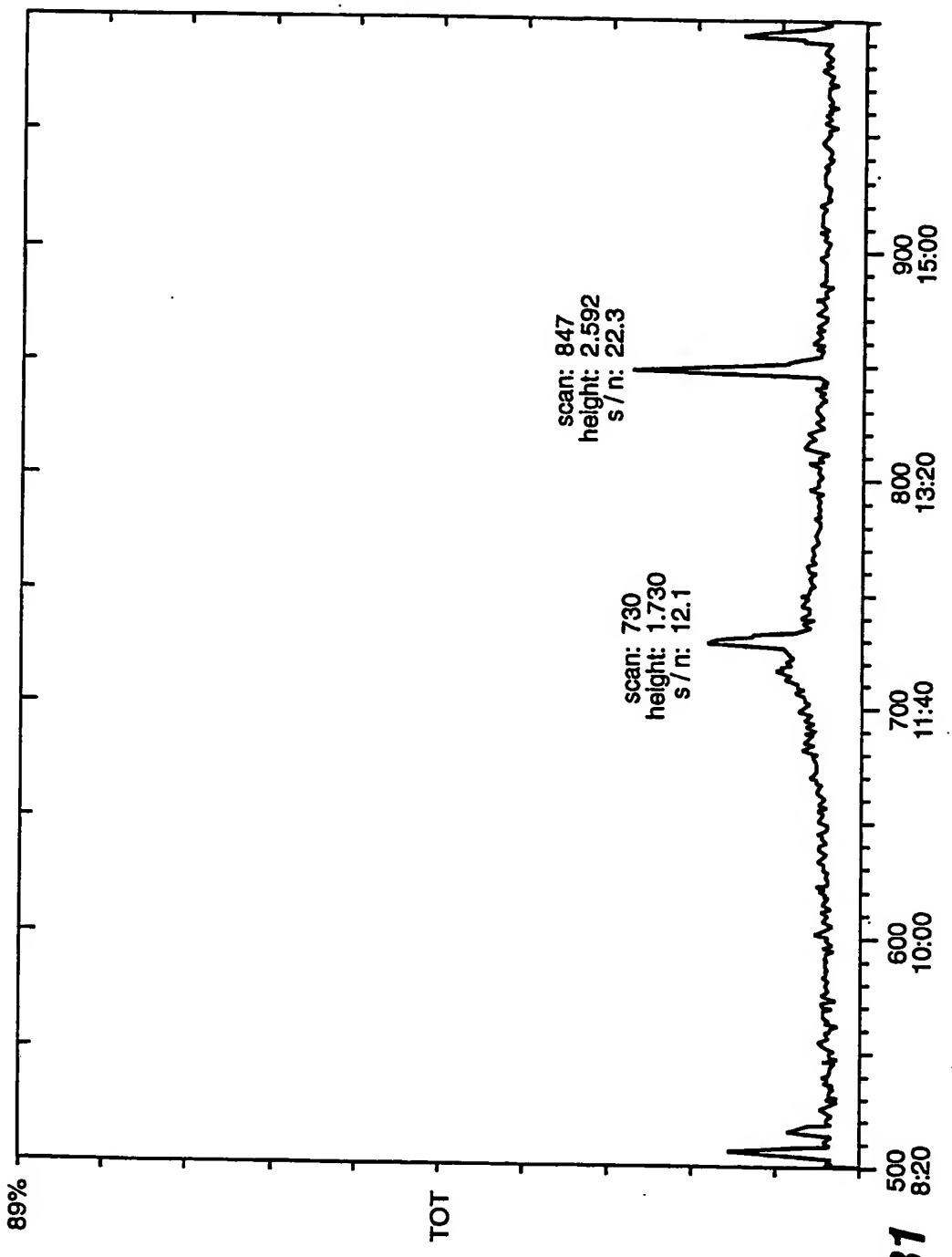
89%
TOT
500
8:20
600
10:00
700
11:40
800
13:20
900
15:00
scan: 730
height: 1.730
s/n: 12.1
scan: 847
height: 2.592
s/n: 22.3

FIG._31

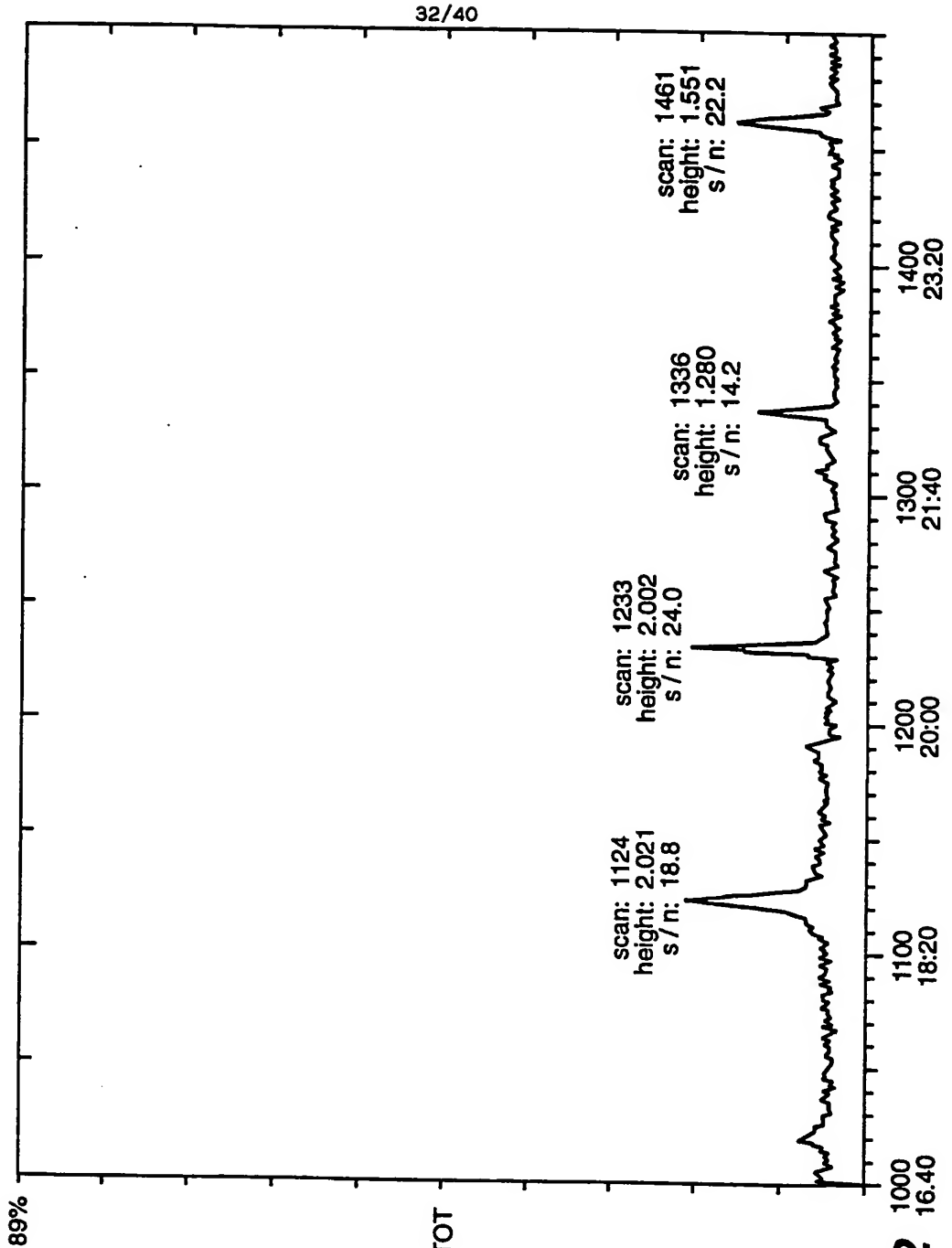

FIG._32

SUBSTITUTE SHEET

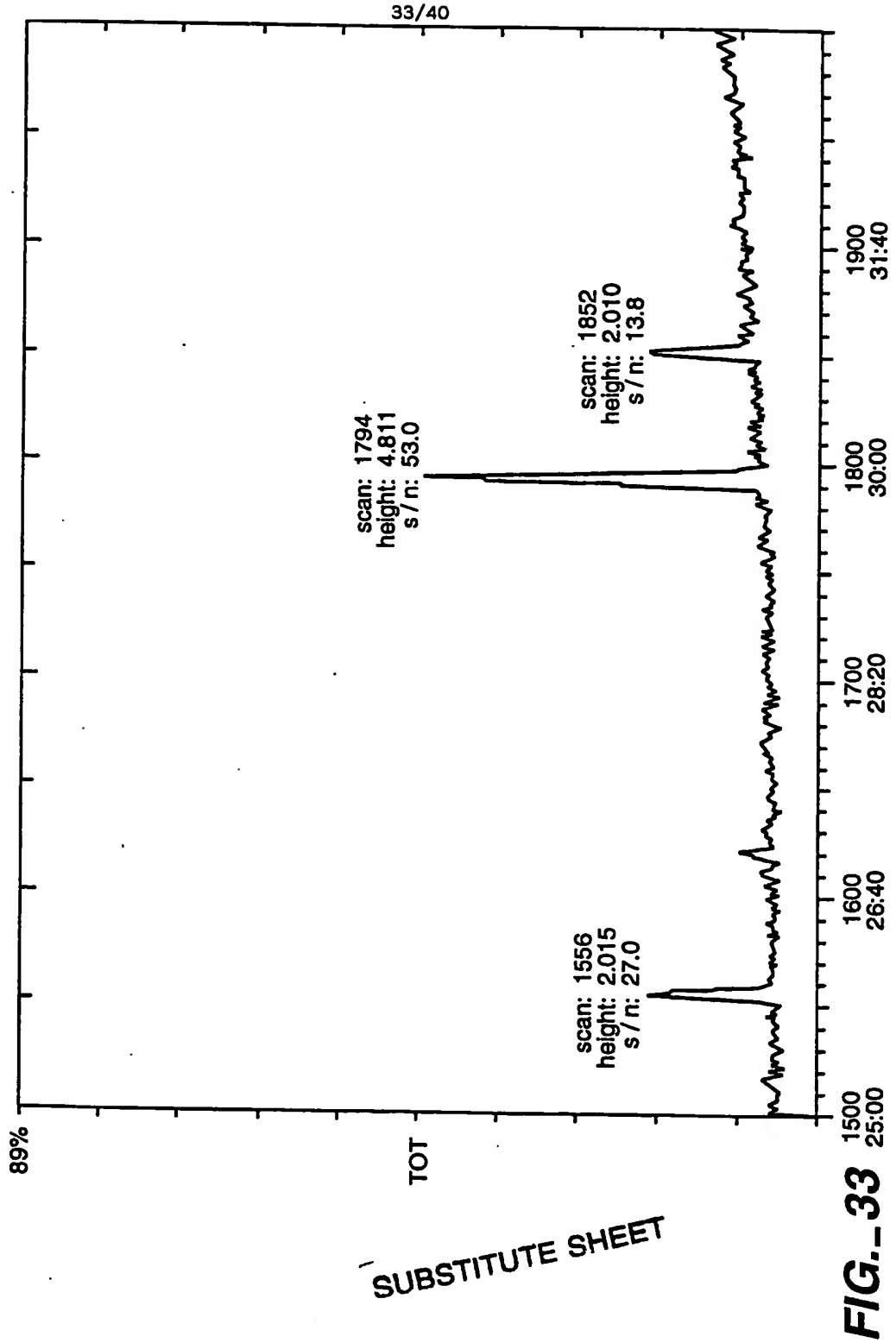

FIG._33

SUBSTITUTE SHEET

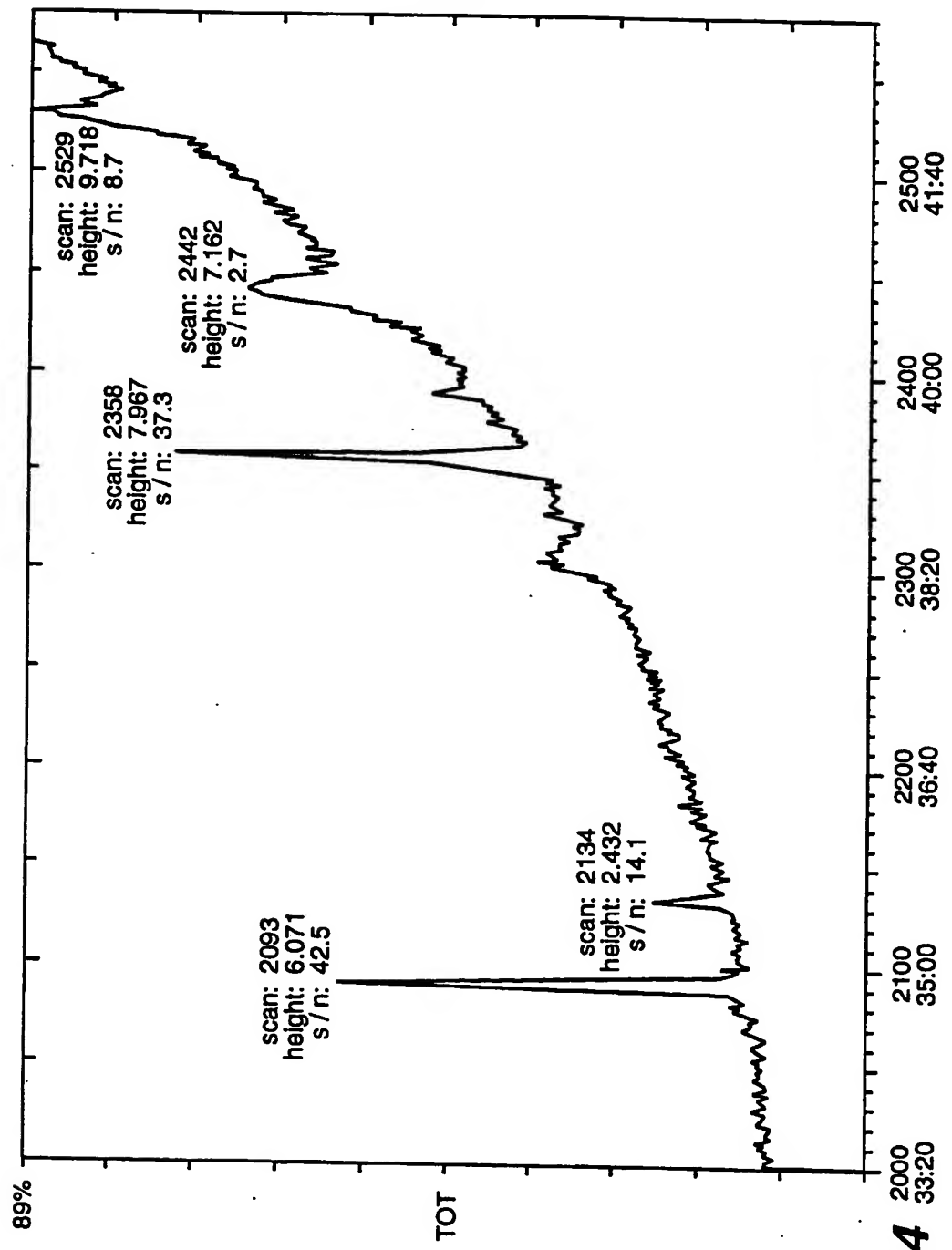
89%
TOT
scan: 2529
height: 9.718
s/n: 8.7
scan: 2442
height: 7.162
s/n: 2.7
scan: 2358
height: 7.967
s/n: 37.3
scan: 2134
height: 2.432
s/n: 14.1
scan: 2093
height: 6.071
s/n: 42.5
2000
33:20
2100
35:00
2200
36:40
2300
38:20
2400
40:00
2500
41:40

FIG._34

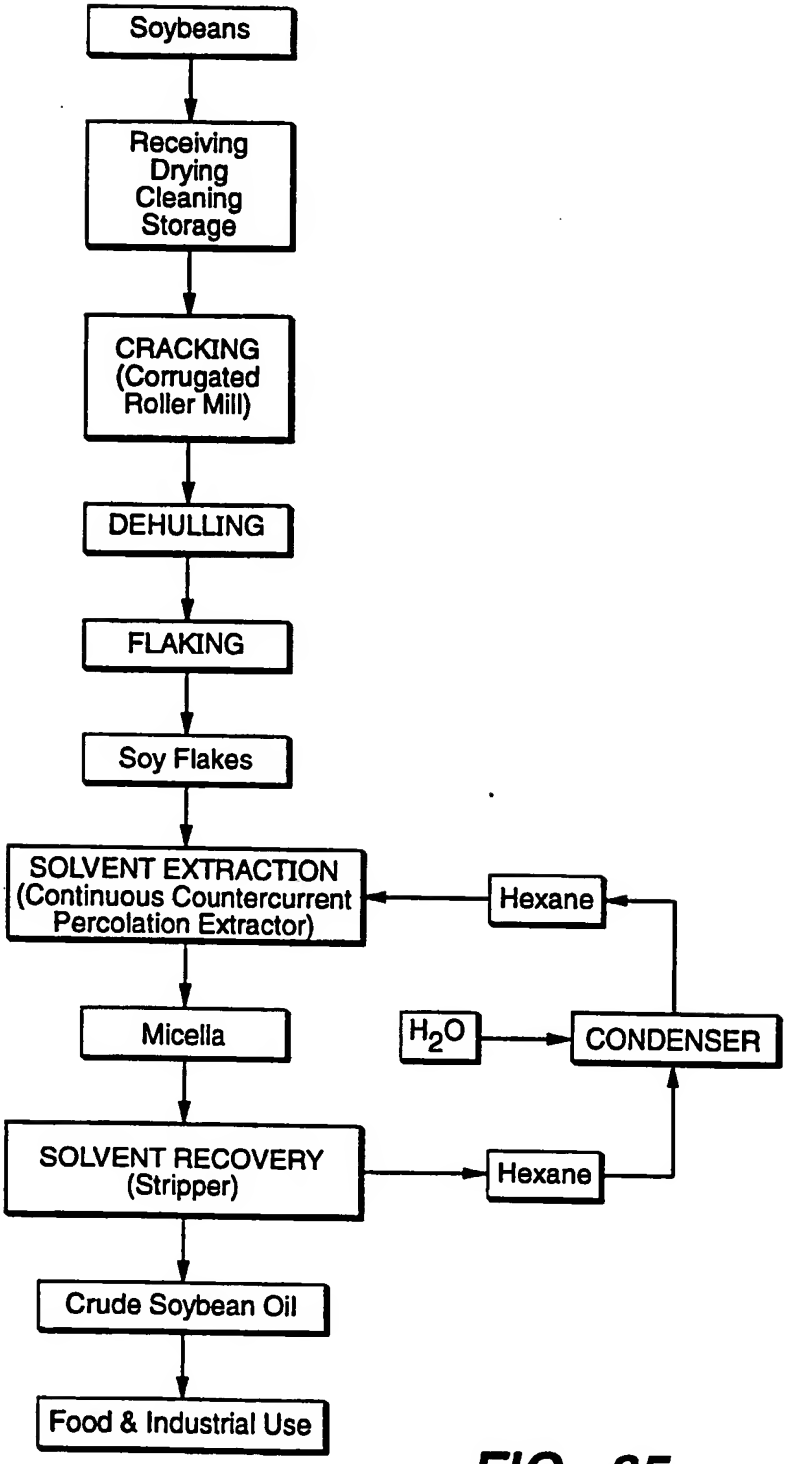
Soybeans
Receiving
Drying
Cleaning
Storage
CRACKING
(Corrugated
Roller Mill)
DEHULLING
FLAKING
Soy Flakes
SOLVENT EXTRACTION
(Continuous Countercurrent
Percolation Extractor)
Hexane
Micella
H_2O
CONDENSER
SOLVENT RECOVERY
(Stripper)
Hexane
Crude Soybean Oil
Food & Industrial Use

FIG._35

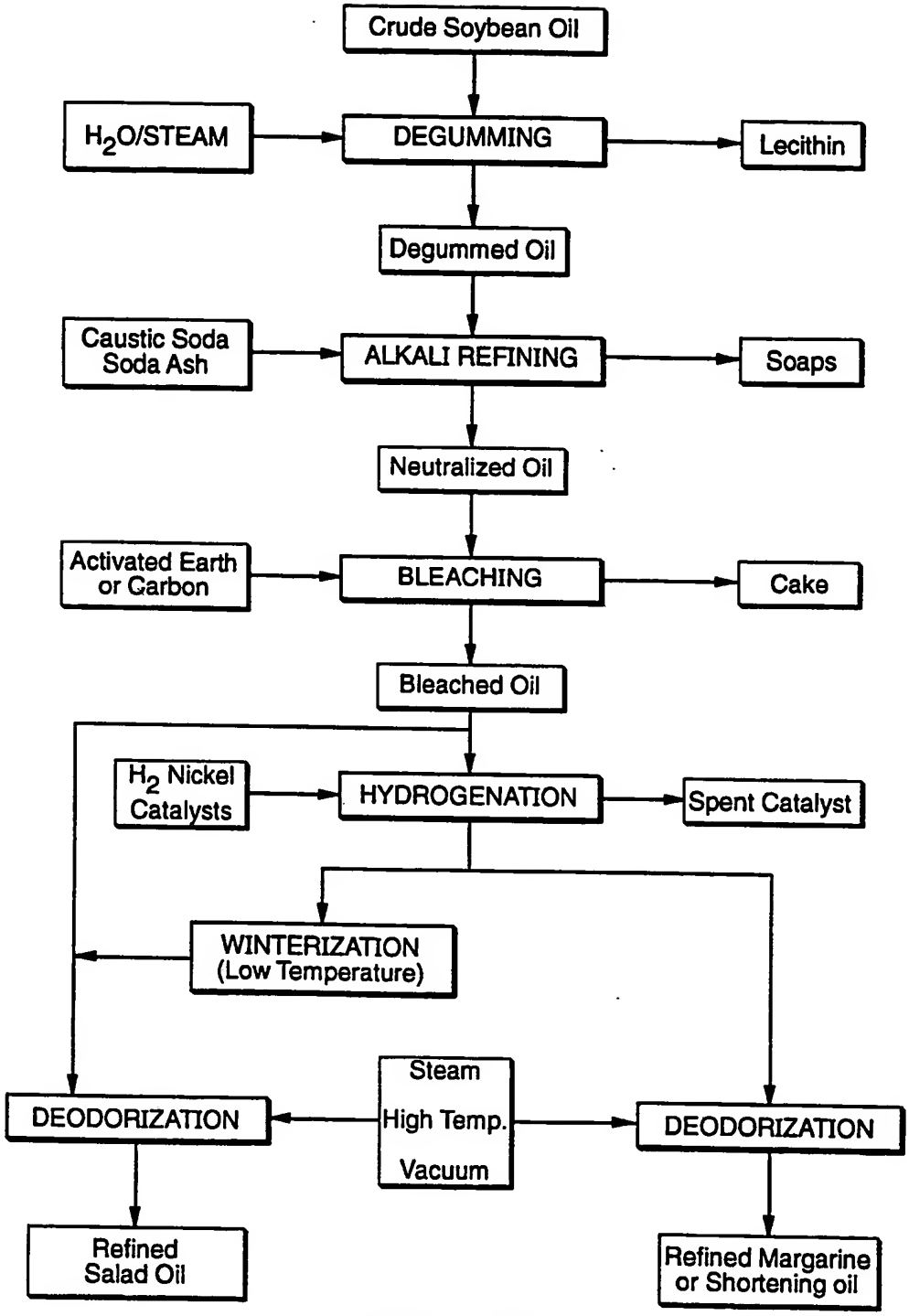

FIG._36

SUBSTITUTE SHEET

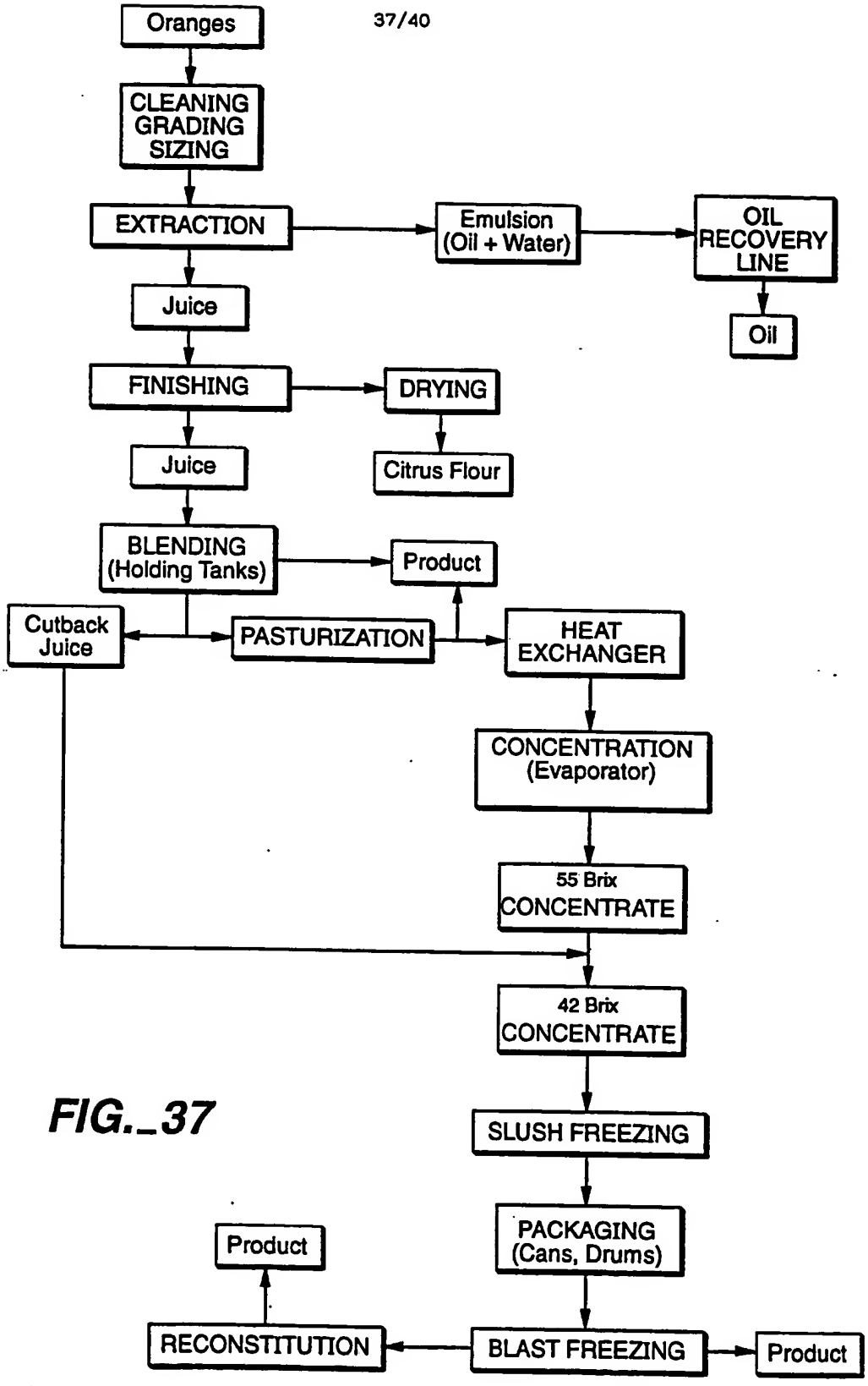
Oranges
CLEANING GRADING SIZING
EXTRACTION
Emulsion (Oil + Water)
OIL RECOVERY LINE
Oil
Juice
FINISHING
DRYING
Citrus Flour
Juice
BLENDING (Holding Tanks)
Product
Cutback Juice
PASTURIZATION
HEAT EXCHANGER
CONCENTRATION (Evaporator)
55 Brix CONCENTRATE
42 Brix CONCENTRATE
SLUSH FREEZING
PACKAGING (Cans, Drums)
Product
RECONSTITUTION
BLAST FREEZING
Product

FIG._37

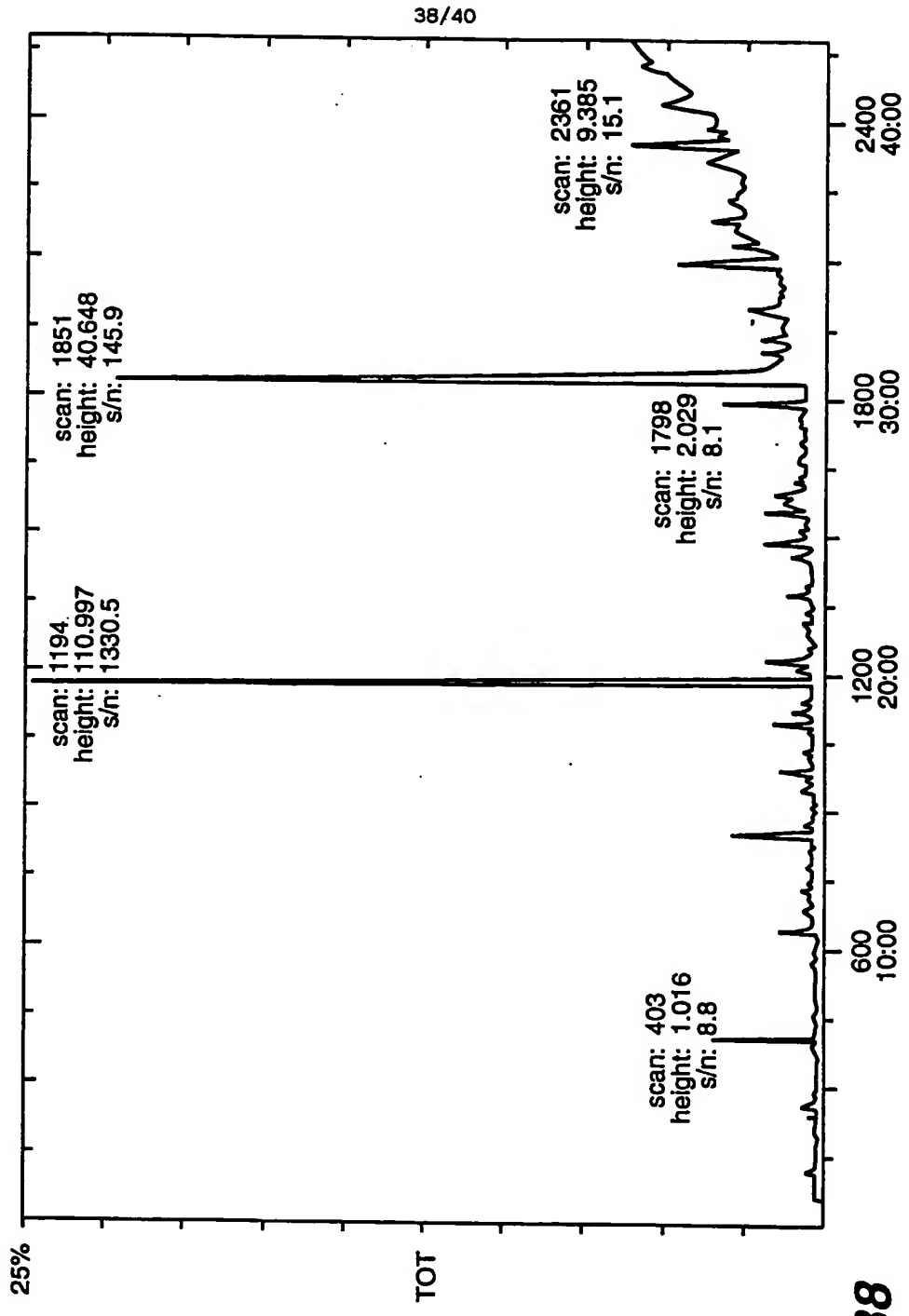
25%
TOT
scan: 403
height: 1.016
s/n: 8.8
scan: 1194
height: 110.997
s/n: 1330.5
scan: 1798
height: 2.029
s/n: 8.1
scan: 1851
height: 40.648
s/n: 145.9
scan: 2361
height: 9.385
s/n: 15.1
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._38

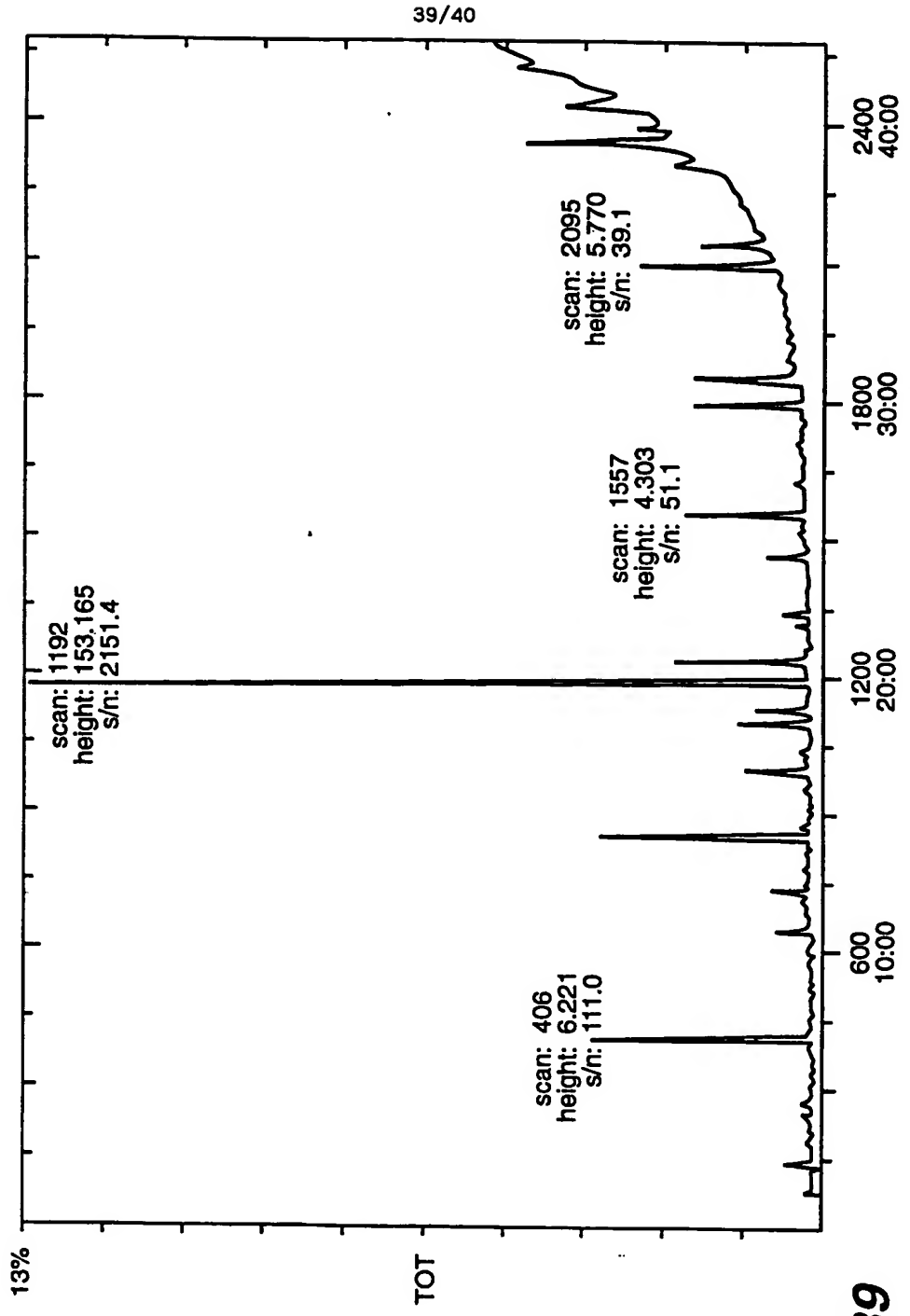
13%
TOT
scan: 1192
height: 153.165
s/n: 2151.4
scan: 406
height: 6.221
s/n: 111.0
scan: 1557
height: 4.303
s/n: 51.1
scan: 2095
height: 5.770
s/n: 39.1
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._39

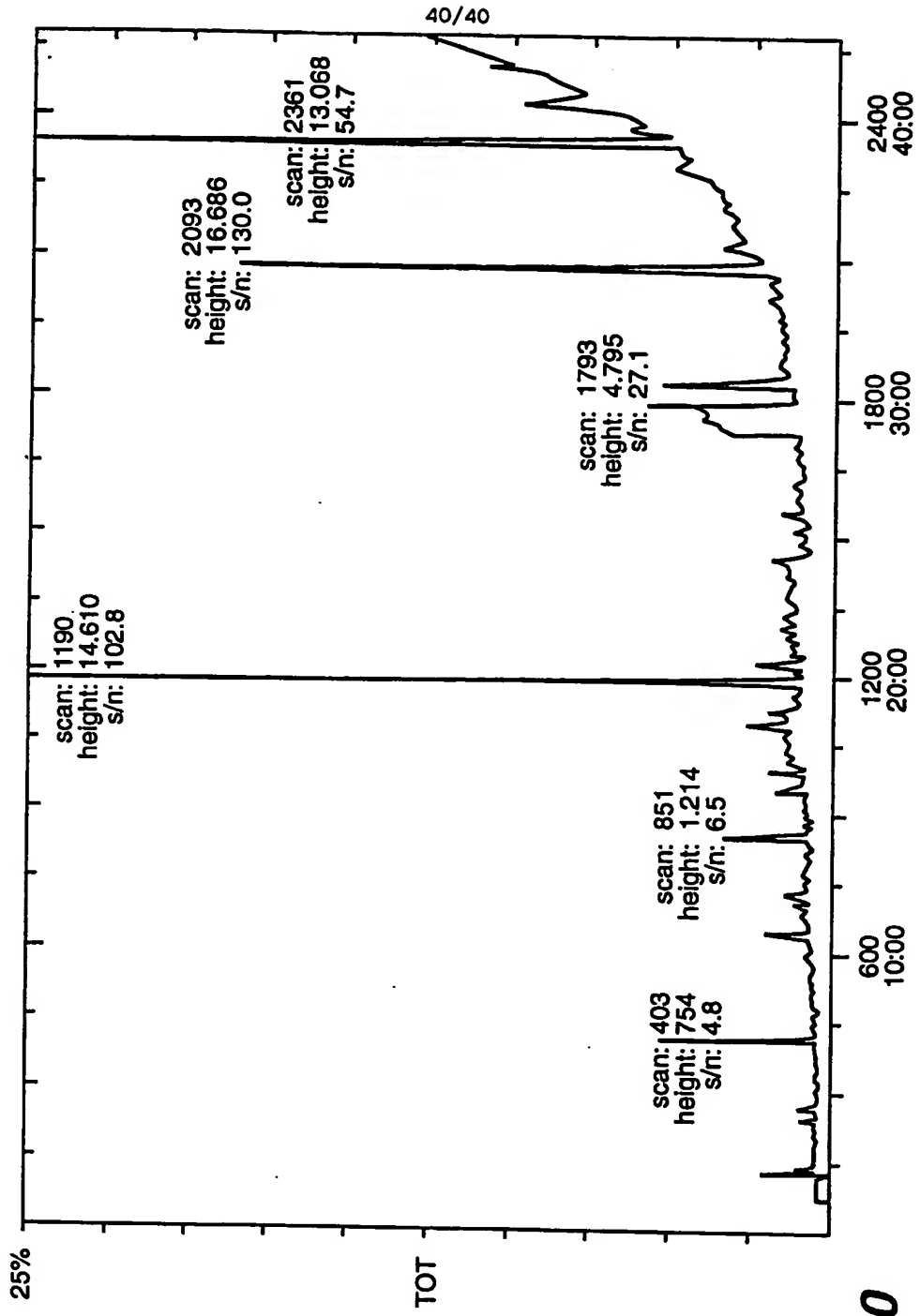
40/40
25%
TOT
scan: 1190
height: 14.610
s/n: 102.8
scan: 403
height: 754
s/n: 4.8
scan: 851
height: 1.214
s/n: 6.5
scan: 1793
height: 4.795
s/n: 27.1
scan: 2093
height: 16.686
s/n: 130.0
scan: 2361
height: 13.068
s/n: 54.7
600
10:00
1200
20:00
1800
30:00
2400
40:00

FIG._40

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